INORGANIC
QUANTITATIVE
ANALYSIS

INORGANIC QUANTITATIVE ANALYSIS

NEW EDITION

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PREFACE

It has been the aim of the authors, in preparing this work, to apply the principles of Physical Chemistry to the theory of Quantitative Analysis in a detailed and thorough manner. In stressing this point of view, it has not been forgotten, however, that the two other aspects of the subject, namely, technique and methods, play an equally important part in the education of the analyst. Accordingly, it will be found that technique has been treated at great length, for it is felt that by so doing both the instructor and the student will be enabled to save the time that otherwise would have to be devoted in the laboratory to a discussion or demonstration of the subject. The methods which have been given in the text will be found sufficient, not only for an elementary course, but for an advanced course as well; they have been selected so as to present something new in theory or technique in every case, and have been arranged with respect to their general order of difficulty, progressing from relatively simple methods to those involving numerous complications.

The historic and purely arbitrary division of the subject into gravimetric and volumetric methods on the basis of the technique used has not been employed. Instead, the development of the subject is based on fundamental principles. The order of presentation has been carefully considered and is as follows: (1) precision, (2) weighing, (3) measurement of volumes, (4) neutralization, (5) solubility product, (6) oxidation-reduction, (7) electrodeposition, (8) evolution and measurement of gases, (9) electrical conductance, and (10) photometry. While any arrangement of this kind is, in a sense, arbitrary, it is felt that there is sound logic in putting neutralization before solubility product because, in the former, the student becomes well acquainted with the subject of hydrogen ion concentration, a factor which enters into all analytical procedures and, therefore, demands attention from the very outset.

[v]

Examples are appended to each chapter. These examples are of a practical nature and illustrate the points covered in the chapters to which they are attached.

The references throughout the book are unusually complete for a work of this nature and will be found of marked convenience, not only to instructors and students, but to the practising analytical chemist. Full citations have been given in each case, and an author index and a subject index have been added to facilitate investigation.

In the make-up of the book, the paragraph numbering system has been used for references, to make easy the assignment of work.

The text contains one hundred and thirty-two illustrations and diagrams. Great care has been taken to make each of these accurate and of a size that is both convenient and clear in every detail. There are also numerous tables, giving physical-chemical and other useful data.

This work is based on "Inorganic Quantitative Analysis" by Professor Harold A. Fales. In preparing the present volume, the authors have striven to preserve the point of view and the general arrangement of material of the earlier work. Many rearrangements of material and additions have been made, however. Among these are the following: The chapter "Apparatus and Reagents" has been combined with the chapter "General Operations," in order to avoid repetition. The chapter "Properties of Aqueous Solutions of Electrolytes," which conforms with the more recent ideas on the ionization of strong and weak electrolytes, has been added, and some of the theoretical discussion formerly in the chapter "Solubility Product Principle" has been transferred to this chapter. In the chapter "Organic Precipitants and Non-aqueous Solvents," a comprehensive table of organic precipitants has been added. The chapter "Oxidation-Reduction Theory" has been almost completely rewritten, using, as the arbitrary zero of potential, the potential of the normal hydrogen electrode. The chapter dealing with electrodeposition has been extensively revised. The chapter "Electrometric Methods" and the chapter "Photometry" have been added. Some of the more complicated mathematical derivations have been transferred to the Appendix. New methods, numerical examples, and explanations of stoichio-

metric calculations have been added. The number of examples at the end of each chapter and the number of illustrations and graphs have been greatly increased. The list of reference books has been enlarged and references have been brought up to date.

The authors are greatly indebted to Professor A. C. Hardy of the Massachusetts Institute of Technology and to his collaborators for their generous permission to reproduce in the chapter on photometry some of the graphs appearing in their very excellent book, "Handbook of Colorimetry," published by Technology Press, Cambridge, Massachusetts. These graphs are shown in Figures 116, 118, 120, 121, 130, and 131.

The authors are indebted also to Dr. Alexander Knoll of the Department of Chemistry at Columbia University and to Dr. Marcel Droz of Washington Square College, New York University, for many valuable suggestions and criticisms.

The authors wish to express their thanks to D. Van Nostrand Company, Inc., for permission to reproduce the graph given in Figure 101; to Christian Becker, Inc., for permission to reproduce the drawing shown in Figure 29; to Eimer and Amend, Inc., for permission to reproduce the photograph shown in Figure 27; to Leeds and Northrup Company for permission to reproduce the material shown in Figure 94; to Pfaltz and Bauer, Inc., for permission to reproduce the photograph shown in Figure 28, and to Carl Zeiss, Inc., for permission to reproduce the drawing shown in Figure 129.

Acknowledgment is also made to the host of workers whose articles have been cited and to any others whose work the authors have unwittingly failed to cite or to locate.

The author of the previous edition, Harold A. Fales, wishes to express his particular appreciation of the generous assistance given him in the preparation of that edition by his colleague, Professor Hal T. Beans, whose constructive suggestions and advice, not only with respect to the presentation of the theory, but also with respect to the details of the procedures and to the arrangement of the first edition as a whole, were invaluable. Since the author, as a student, was fortunate enough to come under the tuition of Professor Beans, and later, as a teacher, to be associated with him in the same department, it is only paying the most modest of

tributes to say that a very large part of the spirit of that work was but the natural reflection of this association. The author of the previous edition also wishes to express his thanks to the following for their assistance in the preparation of that edition: Dr. Rocco Fanelli, Mr. Harvey B. Williams, Dr. George Barsky and Dr. Stephen P. Burke.

The authors of the present work will welcome criticisms and suggestions and will be especially grateful to anyone calling to their attention errors which may exist in the text.

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HAROLD A. FALES.
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New York City

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INORGANIC QUANTITATIVE ANALYSIS

CHAPTER I

SCOPE AND NATURE OF SUBJECT

1. General Considerations. — *Quantitative Analysis* has for its object the determination of the quantities of constituents present in a given amount of a compound or mixture. There are many situations in our complex civilization which make such analyses necessary. Not only have the foundations of the science of chemistry been established largely on the basis of the results of quantitative analysis, but further progress in research requires analysis as an important tool. Physics, biology, geology, and other natural sciences likewise have need of the services of the analytical chemist in the solution of important problems. The analytical chemist often plays an important part in the successful operation of an industrial process because the selection of raw materials, the regulation and improvement of the process, and the determination of the usefulness of the products are often made on the basis of the results of quantitative analysis. Applications of quantitative analysis, too numerous to mention, in the fields of pure science, manufacture, mining, agriculture, and medicine serve as evidence of its importance in the life of man and should emphasize the value of a more complete understanding of its principles and practices.

For convenience, it is usual to divide the subject of Quantitative Analysis into two branches. One branch, known as *Inorganic Analysis*, deals with the analysis of various compounds of the metallic and non-metallic elements. The other branch, known as

Organic Analysis, deals with the analysis of compounds of carbon with hydrogen wherein the hydrogen may be replaced entirely or in part with oxygen, nitrogen, chlorine or sulfur. It is with *Inorganic Quantitative Analysis* that this book will deal.

Table 1

Elements Grouped with Respect to Frequency of Their Determination

Very Frequent[1]	Frequent	Occasional	Seldom	Very Seldom
Calcium	Aluminum	Barium	Beryllium	Argon
Carbon	Antimony	Bismuth	Cesium	Dysprosium
Chlorine	Arsenic	Boron	Cerium	Erbium
Copper	Chromium	Bromine	Columbium	Europium
Hydrogen	Nitrogen	Cadmium	Germanium	Gadolinium
Iron	Oxygen	Cobalt	Gold	Gallium
Lead	Tin	Fluorine	Holmium	Hafnium
Magnesium	Titanium	Iodine	Indium	Helium
Manganese	Tungsten	Lithium	Iridium	Illium
Nickel	Vanadium	Mercury	Lanthanum	Krypton
Phosphorus		Molybdenum	Lutecium	Masurium
Potassium		Selenium	Osmium	Neodymium
Silicon		Silver	Palladium	Neon
Sodium		Strontium	Platinum	Niton
Sulfur		Thorium	Radium	Praseodymium
Zinc		Zirconium	Rhodium	Rhenium
			Rubidium	Ruthenium
			Tantalum	Samarium
			Uranium	Scandium
				Tellurium
				Terbium
				Thallium
				Thulium
				Xenon
				Ytterbium
				Yttrium

The materials which are generally encountered in this branch of the subject are acids, bases, salts, alloys (ferrous and non-ferrous), minerals, ores, and occasionally gases. With respect to the frequency with which the several elements are encountered, Table 1

[1] Elements in this column are those usually considered in an elementary course in Quantitative Analysis.

will serve to give a fair idea, although it must be pointed out that the classification is subject to change, since the determination of an element may become a frequent matter because of some local reason or because of some technical or commercial application. Thus, the determination of tungsten and vanadium fall in the frequent class today, whereas two decades ago it was a rare matter to encounter either of these elements.

In general, to effect an analysis, the procedure of the analyst is to prepare a representative sample and then effect its solution by appropriate means. From this point on, the further work of the analyst really divides itself into two quite distinct steps, the first having to do with the isolation of the desired constituent from such of the others as might interfere with its subsequent determination, the second having to do with the actual determination of the desired constituent after the previous removal of the interfering constituents.

Of these two steps, the first is often a very complicated matter involving a considerable knowledge of theory and technique, while the second is, at least in many cases, relatively a simple matter. This difference in the order of difficulties cannot be too strongly emphasized; it might seem that the comprehensive schemes of separation which have been worked out for qualitative analysis would obviate the troubles, but this is only partially true because the qualitative schemes in the main are not precise enough. The general tendency has, therefore, been rather to devise special methods, such methods depending not only upon the particular constituents present but also upon the absolute amounts of the constituents; hence it not infrequently happens that a whole quantitative procedure will have to be abandoned or seriously modified because a sample contains a constituent that has not been provided for by the particular scheme.

An intelligent quantitative analysis presupposes, then, not only a knowledge of qualitative analysis but also more or less specific information as to the approximate composition of the sample. Very often it is possible to gain the requisite information in this latter regard by access to proper references if only the general identity of the sample can be established. Thus, if the sample is a known mineral or ore, some work giving the analyses of minerals,

like Dana's "A System of Mineralogy," [2] should be consulted; if an alloy, some work on the composition of alloys, such as "A List of Alloys," prepared by William Campbell, [3] or "Engineering Alloys," by Woldman and Dornblatt. [4]   If no clue whatever as to the general identity of the sample can be had, then recourse to a qualitative analysis must be made.

In view of the foregoing considerations pointing out the greater difficulty of separations in contradistinction to determinations, it seems preferable for pedagogical reasons to treat of them in inverse order.   We shall, therefore, begin by taking up simple determinations in which interfering constituents are absent, and then gradually work into cases where the necessary separations become a matter of increasing difficulty.

2. Principles Involved in a Quantitative Analysis. — In developing the subject, it seems advisable not to adhere to the traditional treatment of classifying quantitative methods according to the technique employed, as either gravimetric or volumetric, but rather to arrange them according to the physico-chemical principles which are involved.   On this basis, it will be found that the important principles around which we may group most of our quantitative methods are those concerning the following:

1. Neutralization
2. Solubility Product
3. Oxidation-Reduction
4. Evolution and Measurement of Gases
5. Electrical Conductance
6. Photometry

This is the order that will be pursued, and the determinations which have been chosen for the laboratory exercises have been selected with the idea of illustrating these principles, along with the supplemental idea that the exercises introduce the student to something new in laboratory technique each time.

[2] James D. Dana, "A System of Mineralogy," 6th ed., John Wiley & Sons, Inc., New York, 1915.   This work gives the analyses of about 5,500 minerals.

[3] This work gives the composition of about 1,600 non-ferrous alloys.   For more detailed information, consult "A List of Alloys," by W. Campbell, *Proc. Am. Soc. Testing Materials*, **30**[1], 336 (1930).

[4] Woldman and Dornblatt, "Engineering Alloys."   For reference see § 11.

3. Precision. — By precision we mean the narrowness of the limits between which we assume the true value of a measured quantity to lie. The narrower these limits, the higher the precision. There are limits to the precision with which a quantitative determination can be made. The reason for this is to be found in the fact that every analytical method is attended with certain sources of error, among which are incompleteness of precipitation, contamination of the precipitate by impurities, and incompleteness of oxidation or reduction, and it is not possible to eliminate entirely such errors. The precision of a determination can be affected to some extent by the method selected, the equipment used, and the time and effort put forth in carrying out the work. In any case, the precision attempted should fit the requirements of the analysis in hand. For further details about the factors which enter into precision, the reader must be referred at this juncture to Chapter III.

4. Literature. — The habit of looking up original articles and consulting the literature pertaining to the subject should form just as much an integral part of an analyst's training as his laboratory work. As a guide in this direction, we have appended at the end of the chapter a list of textbooks, reference works, and journals that will be of service not only to the student but also to the man engaged in analytical practice.

5. Notebook. — There is no index of an analyst's work which does so much to create a favorable impression as a neat, well-ordered and well-kept notebook. The size of the book should not be too small, say not less than 8 x 6 in., and should contain the following information relative to each determination:

> Date
> Purpose
> Observations
> Calculations
> Results
> Remarks

This information should be so compiled that any one familiar with quantitative analysis can read it readily and comprehensibly and

can check the work without hesitancy or without any searching back and forth whatsoever.

The date is much more important in scientific and technical work than most students appreciate, and the student should invariably train himself to place the date on each page of the notebook. The purpose should be stated briefly, much as a running title. The observations should include a clear and concise record of all weighings and volumetric measurements, and have enough description appended so that there can be no doubt as to what was done. All observations should be entered directly in the notebook at the time *and the practice of making notations on loose scraps of paper should never be tolerated for one instant.*   Calculations should follow observations closely enough so that cross-references between the two can readily be made, and especial attention should be paid to the proper use of significant figures, as described below.   The use of logarithms is to be strongly recommended, as long-hand methods of multiplication and division are both wasteful of time and conducive to mistakes and should be resorted to only as an expediency.   The use of the ordinary ten-inch slide rule should be permissible only as a means of checking over the sequence of figures obtained by logarithms, because a slide rule of this size gives a precision of from two to four parts per thousand, depending on the portion of the scale being used, whereas our aim is a precision of one part per thousand.

Results should usually be expressed as percentages.   In this connection, it must be remembered that many substances, such as minerals, ores, clays, salts, etc., contain moisture, and in this case it is customary to report analyses on what is known as the "moisture-free basis," that is to say, the percentages of constituents are calculated to what they would be if the sample were free from moisture.   For this purpose, it is necessary either to dry the sample before analysis or to make a separate determination of the moisture in the sample, as described in Chapter II.   In the latter method, the moisture is figured on the original weight of sample, while the other constituents are figured on the original weight of sample, corrected for moisture.   Thus, to illustrate by an example: 2.0000 g. copper ore lost 0.0484 g. moisture at 105°, while 0.5000 g. of the same original sample yielded 0.0906 g. copper upon analysis.

The percentage of moisture on the original weight of sample is:

$$\frac{0.0484 \times 100}{2.000} = 2.42\%$$

The percentage of copper on the moisture-free basis is:

$$\frac{0.0906 \times 100}{0.500 \times (100\% - 2.42\%)} = 18.57\%$$

The results should accordingly be expressed:

    Moisture (loss upon drying at 105°)   2.42%
    Copper (moisture-free basis)   18.57%

Under remarks should be included any special happening that might have a bearing on the final results obtained, or any comments that might seem pertinent to the technique or the theory of the method employed.

The importance of keeping a notebook which shall be well-ordered and precise in its record of experimentation and dates cannot be too strongly emphasized. In the famous case of Edwin H. Armstrong *et al.* vs. De Forest Radio Telephone and Telegraph Co. (279 F., pp. 453–4),[5] which involved millions of dollars, the case was won by Armstrong and lost by De Forest on the merits of the respective notebooks. Judge Mayer, in delivering the Court's decree, said:

"It is not practicable to discuss the testimony in all its elaborate detail. . . . On the one side is an enthusiastic, never-say-die young student (Armstrong), with but one thought possessing him. He not only discloses to many persons his belief that he has invented something worth while, but he produces his apparatus, and he produces a sketch which is extraordinary for its clear and unmistakable description to one skilled in the art, and the date of that sketch is incontrovertibly fixed.

"On the other side is a then experienced and able worker in the art, experimenting along certain lines, who is unable to rely solely on notebook entries, which are not clear, but require construing, and who supplements these entries by recollection which is fallible,

[5] Tried before Justice Mayer in the U. S. District Court, Southern District, New York, May 17, 1921.

and not certain. If De Forest, in 1912 or 1913, invented the feed-back circuit, the obvious financial reward in store for him would have induced him, notwithstanding all his difficulties, to do one of two things: (1) that which Armstrong did, that is, in some way make a clear memorandum and have somebody know about it; or (2) file an application for a patent in the same way that during the period concerned he filed many other applications.

"Holding then that Armstrong is the first inventor, and that his claims in suit should be construed as he contends, the sole remaining question is that of infringement."

The decree for the plaintiff was affirmed in the Circuit Court of Appeals, March 13, 1922 (280 F., p. 584).

6. Reports. — In making out reports, the analyst should always bear in mind the fact that the report which he submits binds him to *full responsibility*. If it subsequently turns out that he has made a mistake in calculation, he is none the less liable than if the mistake had been made by adding the wrong reagent or using the wrong indicator. With respect to the responsibility which attaches to the report of an analysis, the Supreme Court of New York in the case of Arthur L. Richards and Robert M. Boyd, Jr. vs. Stillwell & Gladding Incorporated,[6] said in its charge:

"It appears that the defendants — or the defendant, it being a corporation — is a chemical concern, and that for hire it makes assays of metals submitted to it and issues reports to the parties seeking such examination. There is no dispute that on the 10th of February, 1917, after being retained by the plaintiffs to examine certain metal or ore, the defendant issued certain certificates to the plaintiffs that showed that the samples of ore that had been submitted to the defendant showed forty-one per cent plus, of zinc. . . . It is immaterial under what circumstances the defendant issued the certificates. The important question for you to determine is: Did the plaintiffs rely upon the certificates issued by the defendant? If they relied upon them and acted pursuant to such reliance, *then the defendant is liable for any mistake it may have made in the issuance of the certificates.*"

[6] Tried before Justice Joseph E. Newburger, in Supreme Court, New York County. Trial Term, Part 14, April 12, 1920.

7. **Significant Figures.** — Significant figures are those digits which have been put down to express the numerical measure of a quantity to an extent that does not go beyond the *first* doubtful digit. Thus, if the following significant figures have been put down for a weighing — namely, 1.250 g. — it means that the weight of the object has been determined only to the nearest milligram; in other words, the weight is nearer to 1.250 g. than it is either to 1.249 or to 1.251 g.; with respect to tenths of a milligram, the expression shows that we did not carry the measurement that far. The number of significant figures in the expression is four, since it contains three digits in front of the first doubtful digit.

In the expression 0.0125 g., there are but three significant figures, because there are only two digits in front of the first doubtful digit, the zeros which are used in this case serving merely to fix the decimal place. A zero when so used is not a significant figure, since the position of the decimal point in any measurement is determined solely by the unit in which the measurement is expressed.

In 12,500 g. there are really five significant figures, although it should be noticed with reference to quantities like this, containing one or more zeros beginning at the unit's place and reading toward the left, that they are often carelessly expressed in terms of a unit which is really too small to allow our considering the given value as consisting of all significant figures. Thus the value of a Faraday is given as 96,500 coulombs, which, strictly speaking, would indicate that we are sure of its value to within 1 coulomb, whereas the fact is we know only that the value lies between 96,490 and 96,510 coulombs. If there were such a unit as a kilo-coulomb (1,000 coulombs), we could properly write the value of a Faraday as 96.50 kilo-coulombs. Whenever such a situation arises as illustrated above, and we wish unequivocally to attach a precise significance to the value, some deviation measure or explanatory note should be given in the text. Since the first zero is doubtful, we can write 96,500 ± 10.

In making chemical calculations, it must always be borne in mind that we are dealing with significant figures because the numbers we are handling represent approximations and not exact quantities. For instance, in reading the burette shown in Figure 1, there is no uncertainty connected with the first three significant

figures, 23.4 ml.[7] The fourth figure, which is determined by esti-
mation, might be recorded as 5, 6, or 7 by different observers, due
to the differences in positions from which they viewed the lower
edge of the meniscus of the liquid.   Obviously, the fourth is a
doubtful figure.   The burette reading may be recorded as 23.46 ml.,
which should be taken to mean that as far as can be observed, it
is closer to this value than to either 23.45 or 23.47.   Calculations
involving approximations must not be extended beyond a point
which is warranted by the
number of significant figures,
the rule in this regard being
that in the operations of
multiplication and division,
the final result can contain
no more significant figures
than the least number of sig-
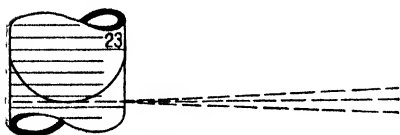
Fig. 1
Significant   Figures   in   a   Burette
Reading

nificant figures entering into the calculation.[8]   Thus, suppose that
in the analysis of an iron ore there was used 0.3087 g. of sample
and that this required for titration 35.23 ml. of permanganate
solution, 1 ml. of which was equivalent to 0.005427 g. of iron.
The percentage of iron is given by the expression

$$\% \text{ Fe} = \frac{35.24 \times 0.005427 \times 100}{0.3087}$$

which, so far as arithmetic is concerned, could be evaluated to any
number of figures, giving

$$\% \text{ Fe} = 61.95253 \ldots \%$$

but which so far as the number of significant figures is concerned
should be evaluated to only four figures, giving

$$\% \text{ Fe} = 61.95\%.$$

In the operations of addition and subtraction, the last digit
retained in the result should correspond to the first doubtful digit

[7] ml. is the abbreviation for milliliter.   A milliliter is one thousandth of a
liter.   For the distinction between milliliter and cubic centimeter see § 103.

[8] In general, for our work, this statement holds true.   For a rigid investiga-
tion of the subject, see J. W. Mellor, "Higher Mathematics for Students of
Chemistry and Physics," 4th ed., Longmans, Green & Co., New York, 1931.

in any of the terms. Thus, the sum of 0.234 g. and 0.0022 g. should be recorded as 0.236 g. Likewise, if a sample is found to contain 0.62% moisture, then the per cent of dry material in the sample is 100.00 − 0.62 = 99.38%.

If duplicate determinations of a constituent yield 35.41 and 35.65% of the constituent respectively, the mean should be given as 35.5%, as it is evident that the third significant figure is doubtful. However, the duplicate results, 18.96% and 18.92%, can be correctly recorded as 18.94%, as the third significant figure is not doubtful. In general, in reporting final results, when the second doubtful figure is 5 or more, it is dropped and the first doubtful figure is increased by 1, and when the second doubtful figure is less than 5, it is simply dropped. When a result obtained by calculation is not final but is to be used in subsequent calculations, the second doubtful figure should be retained.

8. Logarithms. — Since as a usual thing the quantities entering into the computations of the analyst are represented by four significant figures, the great superiority of logarithms[9] over the ordinary long-hand process of multiplication and division is well illustrated by carrying out under each of these two methods the operations necessary in connection with the example already used, namely, in evaluating the ratio. '

$$\% \, \mathrm{Fe} = \frac{35.24 \times 0.005427 \times 100}{0.3087}$$

We have, by multiplying out and dividing in the ordinary way:

0.005427	0.3087)19.124748(61.95
35.24	18 522
21708	6027
10854	3087
27135	29404
16281	27783
0.19124748	16218
100	15435
19.124748	783

[9] Five-place logarithms should be used.

whereas, by logarithms, we have:

$$\log 0.005427 = 7.73456 - 10$$
$$\log \quad 35.24 = 1.54704$$
$$\log \quad\quad 100 = 2.$$
$$\overline{\quad\quad\quad\quad\quad\quad 11.28160 - 10}$$
$$\log 0.3087 \quad = 9.48954 - 10$$
$$\overline{\log 61.95 \quad\quad = 1.79206}$$

9. Chemical Factors. — The calculation of the weight of constituent in a given precipitate follows directly from the proportion:

$$M_nA_p : nM :: \text{weight of precipitate} : x$$

where M_nA_p represents the molecular weight of the precipitate; M, the atomic weight of the constituent or radical desired; and n, the number of atomic weights of M in the molecular weight M_nA_p.

Thus, suppose it is required to calculate the weight of iron in 0.6523 g. of ferric oxide. We would have from the stoichiometric equation that

$$Fe_2O_3 : 2 \, Fe :: 0.6523 \text{ gram} : x$$
$$159.68 \quad 2 \,(55.84)$$

which, upon solving, gives $x = 0.4562$ g. Fe.

Instead of evaluating proportions like the above each time, we can arrive at the result by one multiplication, if we multiply the weight of precipitate by that number which represents the weight of constituent corresponding to one gram of precipitate. Such a number is called a *chemical factor*. For instance, the factor for Fe in Fe_2O_3 is 0.6994 and if, in the above example, we multiply 0.6523 by this number, we get 0.4562, which is the same result we obtained by solving for x in the proportion 159.68 : 2(55.84) :: 0.6523 : x.

As an example to show how we calculate a chemical factor, let us calculate the factor of Na which is sought, in terms of NaCl found. We have by virtue of the stoichiometric relationship between Na and NaCl, that

$$\frac{\text{Atomic weight of Na}}{\text{Molecular weight of NaCl}} = \frac{23.00}{58.46},$$

which upon solving gives 0.3934 as the value of the ratio, and this value is the chemical factor. It will be seen that the factor, multiplied by 100, gives the percentage of Na in NaCl, *viz.*, 39.34%.

10. Examples.

1. Calculate the following factors and keep them for subsequent use.

Found	Sought	Factor	Found	Sought	Factor
$AgCl$	Cl		$Mg_2P_2O_7$	P	
$BaSO_4$	Ba		$Mg_2P_2O_7$	P_2O_5	
CaO	Ca		$PbSO_4$	Pb	
Fe_2O_3	Fe		$BaSO_4$	S	
H_2O	H		$BaSO_4$	H_2SO_4	
K_2PtCl_6	K_2O		$BaSO_4$	K_2SO_4	
K_2PtCl_6	KCl		$BaSO_4$	Na_2SO_4	
$Mg_2P_2O_7$	MgO		SnO_2	Sn	
$Mn_2P_2O_7$	Mn		$ZnSO_4$	Zn	
$Ni(C_8H_{14}N_4O_4)$	Ni		$ZnNH_4PO_4$	Zn	

2. Calculate the percentage composition of the following compounds:

Ans.

(a) Magnesium pyrophosphate

$$\begin{cases} Mg - 21.84\% \\ P - 27.86\% \\ O - 50.30\% \end{cases}$$

(b) Potassium chlorplatinate

$$\begin{cases} K - 16.08\% \\ Pt - 40.15\% \\ Cl - 43.77\% \end{cases}$$

(c) Zinc ammonium phosphate

$$\begin{cases} Zn - 36.63\% \\ N - 7.85\% \\ H - 2.27\% \\ P - 17.39\% \\ O - 35.86\% \end{cases}$$

3. In the course of a quantitative determination, the following data were recorded. In each case the last figure recorded was the first doubtful figure.

(a) 0.0710 g.
(b) 20.03 ml.
(c) 42.30 mg.

How many significant figures does each item contain?

4. Calculate the per cent of iron in a sample when:

$$\frac{40.22 \times 0.005234 \times 100.0}{1.02} = \% \text{ Fe.}$$

5. A sample of copper ore weighing 1.0630 g. is found to contain 0.3066 g. Cu. The ore contains 0.58 % moisture. Calculate the per cent of copper in the ore on the moisture-free basis.

6. A sample of anhydrous $CaCl_2$ yielded on analysis 0.1242 g. CaO. Calculate the weight of Ca in the sample.

7. The weight of magnesium pyrophosphate obtained from 1.1546 g. of sample rock was 0.0432 g. Find the percentage of MgO.

<div align="right">Ans. % MgO = 1.35%.</div>

8. 1.0001 g. of a sample of disodium phosphate yielded 0.6172 g. of magnesium pyrophosphate. What was the percentage of PO_4 in the sample?　　　　　　　　　　　　　　Ans. % PO_4 = 52.67%.

9. The combined weight of the sodium and potassium chlorides from 0.6066 g. of a sample of rock was 0.0318 g. The weight of the potassium chlorplatinate from the combined chlorides was 0.0681 g. What was the per cent of potassium oxide and sodium oxide in the rock?

<div align="right">Ans. % K_2O = 2.17%.   % Na_2O = 0.95%.</div>

10. 1.0005 g. of a mixture of salts containing potassium sulfate, sodium chloride and sodium carbonate yielded 0.5380 g. barium sulfate. A separate portion of the sample lost 1.46% of its weight when dried at 105°–110°. What was the percentage of potassium sulfate on the original and on the moisture-free basis?　　　　Ans. 40.14%. 40.74%.

11. A sample of ore contained 18.35% of lead, 12.68% of zinc, and 15.22% of water. What were the percentages of lead and zinc on the moisture-free basis?　　　　Ans. Pb = 21.63%.   Zn = 14.95%.

12. In the analysis of a zinc-base alloy, 0.5280 g. of sample was dissolved in acid, and the solution submitted to analysis. Using all of the solution, the following results were obtained: copper (electrolytically), 0.0044 g.; $PbSO_4$, 0.0078 g.; SnO_2, 0.0376 g. The solution was then divided into two aliquots, the one giving Al_2O_3, 0.0679 g.; the other giving $ZnSO_4$, 0.5143 g. The iron was determined in a separate sample and found to be 0.10%. Calculate the respective percentages of the metals determined.

<div align="right">Ans. Pb, 1.01%; Cu, 0.83%; Sn, 5.60%; Fe, 0.10%;
Al, 13.64%; Zn, 78.88%.</div>

13. A sample of coal yielded 8.36% of water at 85°. Upon analysis, this partially dried sample yielded 2.32% of moisture and 1.36% of sulfur. What were the percentages of water and sulfur in the original sample?

<div align="right">Ans. H_2O = 10.49%.   S = 1.25%.</div>

14. 1.000 g. of a sample of moist marble lost 0.0210 g. at 110° and 0.4390 g. more on ignition at red heat. What is the probable percentage of water in the original sample?　　　　　　　　　Ans. 2.1%.

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CHAPTER II

12. Laboratory Technique. — The general operations with which the analyst has to deal are, in their usual order of occurrence: sampling, weighing, measuring volumes, solution, fusion, evaporation, precipitation, digestion, filtration and washing, ignition and drying. These operations will be discussed in detail in the following paragraphs except the discussion of the topics of weighing and measuring volumes, which, on account of the extensiveness of detail, will be expanded into separate chapters.

It is to be remarked at this juncture that the key-note to the accomplishment of results in quantitative analysis is not haste in carrying through these operations individually but rather the careful planning of work so that two or more operations are being conducted or are taking place simultaneously; thus while one precipitate is being washed another is being ignited, or while a precipitate is cooling in the desiccator, a weighing is being made. It will soon be found that there is really no such thing as "speed" in quantitative analysis; it is careful planning and thoughtful coördination that bring results. The important thing is not to be required to repeat a determination, and in this respect the observance of certain points will do much toward cutting down the chances of a repetition. The desk should at all times be kept scrupulously clean. It is a good plan to begin the day's work by wiping off the desk with a wet sponge or cloth and to close the day's work the same way. All apparatus not in use should be cleared off the desk, cleaned at once, and put away, while samples, precipitates, filtrates, and all solutions should be marked systematically by means of a marking crayon or small labels so that no confusion may arise as to their identity. In brief, systematic orderliness and cleanliness are the two watchwords of accomplishment.

13. Sampling. — It is of the utmost importance that the sample submitted to analysis should have a composition which is

sensibly the same as the average composition of the original mass from which the sample was derived; otherwise the results of analysis will not give the true percentages of the constituents in the original mass. The object of samplmg is to obtain a sample any portion of which shall have a composition truly representative of the average composition of the original lot. It cannot be too strongly stressed that an analyst should always assure himself of the history of the sample submitted to him and make certain that the precision of the sampling is sufficient for the particular purposes of the analysis.[1]   If he is not certain of this point, he should direct the taking of a new sample or else attend to it himself.

If materials were strictly homogeneous in their composition, that is, if for every specimen all the small unit masses into which we might imagine each specimen to be divided showed precisely the same composition, the problem of sampling would be easy, because then it would make no difference which particular portion we took since its composition would be the same as that of the lot. It rarely happens in practice that materials are homogeneous, hence a portion withdrawn from one part of a lot will not have the same composition as that withdrawn from another part, and neither portion will be representative of the lot. Thus, to cite a few illustrations: minerals, metals, alloys, and other products which have solidified from the molten state almost invariably show a segregation of their constituents; chemical salts are seldom free from the effects of their deliquescent or efflorescent properties; liquids will often show a variability in their composition due to the loss of some volatile constituent; mixtures of gases, particularly flue gases, will often show a great non-uniformity, owing to lack of sufficient time for the several gases to interdiffuse among themselves thoroughly.

By drawing a goodly number of portions in a systematic manner from different parts of the lot and combining them, it is possible to obtain a sample whose average composition will approach very closely to that of the lot. The number of portions to be

[1] Brunton, *Trans. Am. Inst. Min. Eng.*, **25**, 827 (1895); Lundell, Hoffman and Bright, "Chemical Analysis of Iron and Steel," John Wiley & Sons, Inc., New York, 1931; Scott, "Standard Methods of Chemical Analysis," 4th ed., Vol. 2, p. 1003, D. Van Nostrand Co., New York, 1926.

drawn and their relative size depend upon two things: the non-homogeneity of the lot and the precision with which the sample is to represent the lot; the more the non-homogeneity of the lot and the more the precision required, the greater the number of portions that must be taken and the greater their relative size. In the absence of specific data as to the non-homogeneity of a lot, but assuming a fair degree of homogeneity, and assuming further that the composition of the sample shall represent the average composition of the lot to a precision of one part per 1,000, the analyst may take the following directions as a general guide. The number of portions withdrawn from the lot shall not be less than twenty; they shall be approximately of the same size and shall represent regions of uniform spatial distribution in the lot; their aggregate mass with respect to the original lot should never be less than 1/100. If it is convenient to obtain a larger ratio, so much the better, although it is seldom that a ratio greater than 1/20 is ever employed.

The sample so collected will approximate very closely in its average composition that of the lot, but, like the lot, it will be non-homogeneous. It, in turn, might serve as a source for a second smaller sample by the method outlined above, but in order to procure an ultimate sample that will be uniform in every sub-portion, the preceding sample must be made as homogeneous as possible before a further sample is drawn from it. For solids this means successive subdivision and intermixing of the particles or pieces; for liquids and gases it will naturally mean just thorough intermixing as the subdivision already exists.

For the subdivision of friable substances various instruments are used: where the pieces range in size from 2 in. diameter down to 1/8 in. diameter, jaw crushers operated by power will be found very serviceable or, if the quantity of material is small, a chilled steel muller may be employed; for sizes under 10 mesh, say down to 200 mesh, small pebble mills operated by power are to be preferred; for small quantities of material, steel or agate mortars work very nicely. It should be noted that a particle is considered to be 10 mesh when it is just small enough to pass through a standard screen having ten wires to the inch. Likewise, a 200 mesh particle will just pass through a screen containing 200 wires

to the inch. It is to be remembered that any operation of sub-
division always introduces more or less impurity into the sample
from wear of the grinding instrument. The size to which the
subdivision is carried depends upon the weight of the sample.
Thus, to quote the figures of Bailey, *Ind. Eng. Chem.* **1,** 161 (1909),
for the sampling of coal to a precision of 1 part per 1,000, the
relationship given herewith is necessary:

Weight of Sample, lbs.	Size, diameter in inches
7,500	2
3,800	1.5
1,200	1
460	0.75
180	0.5
40	0.425 (2 mesh)
5	0.20 (4 ")
0.5	0.1 (8 ")
0.25	0.076 (10 ")

For intermixing the particles or pieces of a sample the following
devices, among others, are used. If the quantity of material is
large, a pile of it is built up as a cone about a rod as a center. The
material is thrown by shovelfuls on top of the cone in such a
manner that it slides down and distributes itself more or less
evenly over the surface of the cone. After the cone is completed
it is flattened out into a disc or flat circular plate by means of
shovels working from the apex to the periphery round and round
the cone. The disc is then separated into quarters, two opposite
quarters rejected, and the remaining quarters piled up into another
cone, which is flattened out and again quartered. This process
is repeated until the sample is reduced to the proper sized mass,
when it is subjected to further grinding and intermixing.

If the quantity of material is about 5 lbs. or less, intermixing
is accomplished by the method known as *tabling.* This consists
in spreading the finely divided material in the center of a piece
of oil-cloth or paper about 30 in. square and pulling each corner
in succession over to its diagonal partner, thereby causing the mass
of particles to roll over on themselves. The lower portions are
constantly brought to the top of the mass and are intermixed

thoroughly; at the same time an interchange of material between the four quarters of the mass is effected. Each corner is manipulated in turn until the operator has rotated the manipulation around the cloth a sufficient number of times, say at least ten.

After the sample has been made as homogeneous as possible, it is ready to be used in turn to furnish a smaller sample if necessary. In this second sampling, or any subsequent sampling for that matter, the same circumspection must apply to obtain a representative sample and then to make it homogeneous as applied in the first sampling. The final sample for the laboratory should usually be not less than 25 g., and in many cases larger amounts, even up to 1,000 g., will be required, depending on the purposes of analysis. All samples should be put and kept in air-tight bottles as soon as obtained. Even after the proper preparation of a sample, it should be remembered that the principles of sampling still apply, so that in weighing out the small milligram portions for analysis, the analyst should not dip into the sample at random but should spread the sample out and select from 15 to 20 equisized portions distributed equispatially throughout the mass.

14. Weighing. — The operation of weighing is of fundamental importance in quantitative analysis as all determinations are either directly or indirectly based upon the measurement of the relative masses. For first-class quantitative work, weighing must be made to a precision of 0.1 mg. While the attainment of such refinement is in itself not a matter of great difficulty for the masses ordinarily encountered, there are certain details which must be carefully observed and certain errors which must be studiously avoided. As these cannot be adequately described in brief, their discussion, along with the general theory of weighing, has been set apart for Chapter IV.

15. Measuring Volumes. — The general problem of measuring volumes is one with which the analyst is concerned almost as frequently as he is with that of weighing, because of the fact that there are so many methods of analysis which employ the procedure known as *titration*. By this method of analysis the constituent sought is not precipitated and weighed but is determined by allowing a solution of known composition to react with it, and from the volume of solution used, the amount of constituent

is calculated by the laws of chemical equivalence. With respect to titration methods, it may be mentioned that some of them possess extreme accuracy, while all of them possess the advantage that, for routine work, they are very rapid. In so far as the precision of such methods depends upon the measurement of volumes, it is to be noted that the precision falls off rapidly with the smallness of the volumes employed. This factor of size of volume, however, cannot be considered the sole controlling factor of precision in titration methods, as there are other considerations which enter into the problem. For a discussion of all these the reader is referred to Chapter V.

16. Solution. — In most analyses the next step, after weighing out the appropriate amount of sample, is obtaining its solution. Very often a knowledge of the nature of the substance will indicate at once the necessary procedure, but if such knowledge is lacking, the general scheme is to try the solubility of the sample in water. If any insoluble portion remains, decant off the solution and treat the residue with acid; if any residue remains after the acid treatment, filter off the residue, wash it free of acid, ignite and then fuse it with an appropriate flux.

Treatment with Acid. — For substances other than metals the first acid to try is hydrochloric. If the sample contains reducing substances, the hydrochloric acid should be supplemented by nitric acid or some other oxidizing agent, such as potassium chlorate or bromine water. On the other hand, if the sample contains oxidizing agents, the hydrochloric acid should be supple- mented by some reducing agent, preferably sodium bisulfite added in small portions from time to time.

For metals an oxidizing agent is needed to convert the metal from the elemental to the ionic form. It is usual to employ a mixture of nitric and sulfuric acids or to use sulfuric acid and add potassium chlorate (caution) in small portions during the process of solution. Certain non-ferrous alloys, particularly those contain- ing tin, tungsten, or chromium, are often very resistant to the acid treatments just described. For such cases the use of hydro- fluoric acid with nitric acid in the following manner is recom- mended. The weighed portion of the alloy is placed in a platinum dish of 100–125 ml. capacity; next, 10–20 ml. of hydrofluoric

acid is added, and then 0.5 ml. or so of 16 M nitric acid at a time, until about 5 ml. have been added. Often the reaction is very vigorous upon the addition of the nitric acid so that caution must be used in adding this reagent. The efficiency of this method of effecting solution depends upon the fact that fluoride ion forms highly undissociated or complex fluorides with many of the metallic ions.[2] The method carries the disadvantage, however, that the hydrofluoric acid must be removed after solution of the alloy is effected. To accomplish this removal, a few milliliters of 18 M sulfuric acid are added to the solution, and the solution evaporated on the hot-plate until fumes of sulfur trioxide are just about ready to come off. A few milligrams of platinum are always dissolved during this evaporation.

The most effective concentration of acid to use in dissolving substances, either with respect to hydrochloric, nitric or sulfuric acid, is about 9 $M;$ the amount of acid to use is about 2–3 ml. of 9 M acid per 0.1 g. of sample.

17. Fusion. — Substances which cannot be brought into solution by acid treatment must be submitted to fusion. This is generally carried out in a crucible. There are four kinds of fusion ordinarily resorted to, namely:

Alkaline	Oxidizing
Acid	Reducing

The type of fusion and the type of crucible employed depend largely on the nature of the substance and the further purpose of the analysis. The application of these fusions is given in Table 2, along with the particular flux to use, its relative amount, the kind of crucible necessary, and the approximate temperature for the fusion.

In making any fusion there are certain points which should be observed. The substance should be not only in a fine state of subdivision (50 mesh or finer), but should be intimately mixed with the flux by grinding in an agate mortar. The mixture of the substance and the flux should not be put directly into the crucible, but the latter should first receive on its bottom and up its side walls, as far as practicable, a thin lining of the flux alone, as this often reduces the harmful effect of the fusion upon the

[2] Peters, Z. physik. Chem. **26**, 193 (1898).

Table 2

Applications of Various Types of Fusion

Flux	Application	Grams Flux per 0.1 Gram Substance	Kind of Crucible	Temp.
Alkaline Fluxes				
1. Na_2CO_3	Decomposition of silicates Transposition of sulfates	0.6	Platinum	1,200°
2. Na_2CO_3 + MgO	Determination of sulfur in coal		Platinum	
3. $CaCO_3$ + NH_4Cl	Determination of alkalies in rock analysis	0.8 $CaCO_3$ 0.1 NH_4Cl	Platinum	
4. NaOH or KOH	Fusion of oxides of iron and zinc groups for separation of the two groups		Silver	
Acid Fluxes				
5. $K_2S_2O_7$	Conversion of ignited oxides of the iron group, Fe_2O_3, Al_2O_3, TiO_2, etc. to sulfates	1–2	Platinum	300°
6. B_2O_3	Decomposition of certain silicates	2–3		
Oxidizing Fluxes				
7. Na_2CO_3 + $KClO_3$	Ores of arsenic and of chromium		Platinum with great caution	400°
8. Na_2CO_3 + KNO_3	Same as 7			
9. Na_2CO_3 + Na_2O_2	Same as 7		Silver, iron or nickel	500°
Reducing Fluxes				
10. Na_2CO_3 + S	Separation of the precipitated sulfides of Hg, As, Sb, and Sn from CuS	0.4 Na_2CO_3 0.4 S	Porcelain	300°
11. $Na_2S_2O_3$	Same as 10			

crucible. The crucible should be large enough so that it is never more than one-half full and it should always be kept covered. At the start of the heating, a small flame should be used, and the temperature gradually raised until the necessary temperature has been attained. It is not advisable to heat to a much higher temperature than necessary because of the increasing deleterious effect upon the crucible. After the fusion has been effected, which usually takes about sixty minutes, the molten mass should not be allowed to solidify as a solid cake in the bottom of the crucible, but should be distributed in the form of a thin layer around the walls of the crucible by taking the latter in a pair of tongs while the mass is still molten, withdrawing it from the flame and imparting a rotary and tilting motion to it, thereby causing the molten mass to flow up and around the walls of the crucible and to solidify there as a thin layer. This procedure greatly accelerates the subsequent solution of the fused mass. When cool, the crucible is placed on its side in a casserole and covered with water; acid is added or not as the case may be, the casserole covered with a watch-glass, and the temperature raised to 95°-100° and maintained until solution is accomplished.

18. Platinum Crucibles. Use and Care. — Platinum crucibles should have a capacity of about 25 ml. for ordinary routine work and should be supplied with a cover. In using platinum crucibles certain precautions should always be observed, as platinum is very easily damaged. It must be handled with care, or it will soon become dented and distorted on account of its softness. With respect to its chemical behavior, it must be remembered that platinum is attacked even at ordinary room temperatures by strong oxidizing agents, such as nitro-hydrochloric acid (aqua regia), free chlorine and bromine, and at somewhat higher temperatures by ferric chloride. It forms brittle compounds or alloys with free sulfur, phosphorus, arsenic, selenium, etc., with low melting alloys, and also with metals which are easily reduced, particularly mercury, lead, bismuth, tin, and antimony. Hence these elements or their compounds should never be heated or fused in platinum. With respect to strong alkalies, the hydroxides of potassium, sodium, lithium and barium must not be fused in platinum; the use of silver or nickel crucibles is recommended for such

fusions. However, the carbonates of the strong alkalies may be fused in platinum.

When platinum crucibles are heated over a gas flame, they must be kept out of the reducing zone of the flame, because contact with the hot, unburned gases of this zone produces a gray crystallization on the surface of the platinum, and this effect, if not removed by gentle rubbing with a suitable abrasive, will soon spread throughout the crucible and ultimately bring about cracks in it. While being heated, the crucible should be supported upon a platinum triangle or, lacking this, upon a silica or clay triangle; while hot, it should be touched most preferably by platinum-tipped tongs, less preferably by nickel tongs, and never by iron.

Platinum crucibles should be frequently scoured, both inside and out, either with sea sand, Ottawa sand, or some abrasive of the general nature of a rouge. If this treatment fails to remove stains, particularly iron stains, the crucible may often be cleaned by a prolonged fusion of an hour or more with acid potassium sulfate. In this process, the crucible is filled with the flux, the cover put on, and the temperature kept at a point (about 300°) where the fumes of SO_3 just begin to come off. Care must be taken, however, that the available SO_3 is not all driven off, leaving the normal sulfate, as this salt expands so rapidly on cooling that it might break the crucible. Sodium carbonate and borax may also be used as cleaning fluxes. For stains which resist the foregoing treatments, the authors have corroborated the experience of Professor G. H. Walden of the Department of Chemistry at Columbia University, that by leaving the crucible in an electric muffle furnace at a temperature around 1,000° for 14 hours, the iron is brought to the surface, and then, upon digestion with concentrated commercial hydrochloric acid, is, in most cases, completely removed.

19. Evaporation. — The vessels used for evaporation of liquids are glass beakers, porcelain casseroles, and platinum dishes. It must be borne in mind that all kinds of glass are more or less soluble in water and in various solutions, the solubility increasing rapidly with the alkalinity of the solution and with increase of temperature,[3] so that the use of glass beakers should be avoided for evapora-

[3] See P. N. Walker, *J. Am. Chem. Soc.*, **27**, 865 (1905), for composition, solubility, and other behavior of chemical glassware.

tions which are preparatory to a precipitation. For such cases, porcelain casseroles are preferable to glass beakers owing to their lesser solubility, but where the work demands the highest precision, only platinum should be used. In no event should strongly alkaline solutions be evaporated, as even platinum will be attacked under these conditions. Such solutions should first be neutralized or made faintly acid. Solutions faintly alkaline with ammonium hydroxide may be evaporated in porcelain without any sensible solution of the porcelain. In cases where it is necessary to evaporate a solution to dryness, the use of glass is always risky, owing to the likelihood of its cracking when the solution goes dry.

Fig. 2

Glass Loops Used to Permit Escape of Vapors During Evaporation

Porcelain is much safer to use. A detailed study of the dissolving action of various solutions on Pyrex glass containers has been carried out by Walker and Smithers.[4]

During the evaporation of a liquid, it should be protected from anything that might fall into it and, at the same time, the escape of the vapor must not be interfered with. These two conditions can be obtained by taking three or four semi-elliptic U-shaped loops[5] of glass rod and hanging them equidistantly around the rim or edge of the evaporating dish and then placing on top of them a
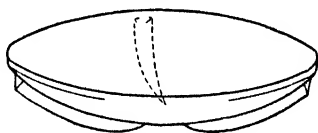
Fig. 3

Watch Glass Provided with Ridges to Permit Escape of Vapors

watch-glass of somewhat larger diameter than the dish, as shown in Figure 2. A watch-glass provided with glass projections on the underneath surface, as shown in Figure 3, is obtainable and serves as a very convenient cover for an evaporating dish.

A container in which it is often convenient to carry out evaporations is a Phillips assay beaker shown in Figure 4.

[4] Walker and Smithers, *Nat. Bur. Standards, Technol. Papers*, No. 107 (1918).
[5] The limbs of the loops should be about 1–1.5 cm. long, have a diameter of about 0.6 cm., and a free distance between them of about 0.6 cm.

Solutions heated over a live flame are prone to bump so that evaporations should generally be conducted on a water-bath or a steam or gas hot-plate.   Evaporations are, at best, time-consuming operations, frequently taking as long as 18 hours; about the only thing the analyst can do to compensate matters is to employ himself with other operations during this time or else arrange matters so that the evaporations take place over night.

Fig. 4
Phillips Assay
Beaker

Certain salt solutions, particularly alkali chlorides, exhibit the phenomenon known as "creeping"; the salt deposits on the wall of the vessel at the surface of the solution and then gradually creeps up the wall and finally over the top of the vessel. This creeping can be stopped by painting a narrow band of collodion around the wall of the vessel a slight distance above the level of the solution.
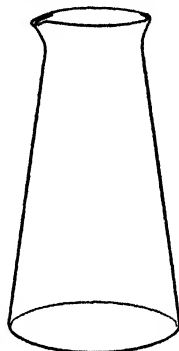
20. Evaporation of Sulfuric or Hydrofluoric Acids. — It is often required to treat a residue or precipitate in a crucible with concentrated sulfuric acid or with a few drops of sulfuric acid and 10–

Fig. 5
Air Bath

15 ml. hydrofluoric acid, and then to get rid of the acids by evaporation. This operation is best accomplished by placing the crucible in an air bath and then maintaining a temperature of about 300°. A very serviceable and suitable air bath for this purpose may be made by taking a silica beaker, a monel metal beaker, or a nickel crucible, about 7 cm. in diameter and 9 cm. deep, and encompassing its upper edge by means of a triangle made of nichrome wire, this device enabling the operator to suspend the beaker from an iron ring. A quartz or platinum triangle with its legs bent at right angles to the plane of the triangle and cut to a length of about 3 cm. is placed inside of the beaker to receive the crucible, as shown in Figure 5. If the full flame of a Bunsen burner is used, a temperature of 350° may be attained inside
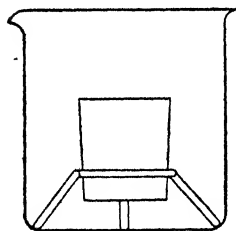
the beaker.   It will be found that an air bath of this description allows a very rapid evaporation without bumping or spattering, occurrences which almost invariably happen if one tries to conduct the evaporations by simply placing the crucible on an asbestos mat which is directly heated by the gas flame.

21. Burners. — The burners used in supplying heat in fusions, evaporations, and other laboratory operations where heat is required, are of two types — the Bunsen or Tirrill type and the Meker type.   These are illustrated in Figure 6.

Bunsen or Tirrill Type. — These burners are capable of producing temperatures up to about 800° and are useful for igniting filter papers and conducting ignitions, fusions or other operations where temperatures not in excess of 800° are required.
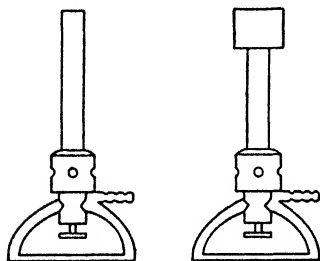
Meker Type. — With this type of burner, a temperature of 1,300° can be reached.   It is particularly useful for igniting precipitates such as silica, aluminum oxide, magnesium pyrophosphate, etc., and for conducting the fusion of refractory silicates.

Fig. 6
Types of Burners

22. Precipitation. — The general theory underlying precipitation will be found in the chapter on the Solubility Product Principle so that we will confine ourselves to certain practical points of technique.   In general, precipitates should be formed by adding the necessary reagent dropwise to the solution with constant stirring so as to prevent the accumulation of any great local excess of precipitant.   The necessary quantity of precipitant to insure quantitative precipitation should be calculated beforehand and not very much more than the calculated amount added, unless otherwise specifically directed.

23. Hydrogen Sulfide Generator. — Hydrogen sulfide is an important precipitant in analytical chemistry.   It is customary now to make hydrogen sulfide precipitations under slight pressure in a rubber-stoppered flask, preferably an Erlenmeyer flask, rather than to allow the hydrogen sulfide to escape into the air from an open beaker or one covered with a watch-glass.   As for the

matter of the slight pressure which is necessary, any form of Kipp generator is suitable; hence it is mostly a question as to the proper sized generator to select in order that the capacity be sufficient for the demands upon it.   For a general routine laboratory, it is advisable to have a fairly large-sized generator always ready for service, but for student work it has been found more satisfactory to provide each student with his own small outfit which he gets ready
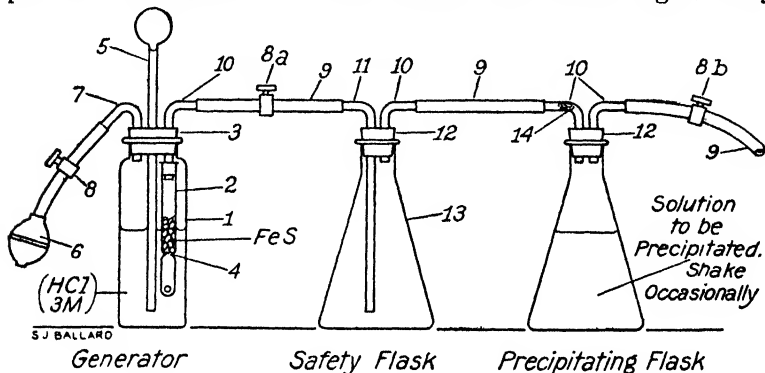
Fig. 7

Banks Hydrogen Sulphide Generator

1 Generator bottle	6 Pressure bulb	10 Glass tube 90° ∠
2 Iron sulphide tube	7 Glass tube 45° ∠	11 Glass tube 90° ∠ long stem
3 3-hole rubber stopper	8 Hard rubber screw clamp	12 2-hole rubber stopper
4 Perforated plate	8a Hard rubber screw clamp	13 Erlenmeyer Flask 500 c.c.
5 Manometer tube	8b Hard rubber screw clamp	14 Plug of cotton wool
	9 Rubber tubing, 5 mm. dia.	

as wanted.   For the student's individual use the generator devised by Mr. Reginald M. Banks, and shown in Figure 7, is suitable.

Directions for Use. — The generator is connected with an empty flask which is to serve as a trap in case any of the solution comes over from the generator; the safety flask is connected with the flask which contains the solution to be saturated with hydrogen sulfide; at 14 it is advisable to place a small plug of cotton wool, as this substance will mordant out any ferrous chloride that has been carried along with the hydrogen sulfide gas stream by entrainment. The hard rubber screw clamp 8*b* is opened and hydrogen sulfide allowed to displace the air in the safety flask and in the precipitating flask.   The screw clamp is then closed and air is pumped

into the generator until a slight pressure is indicated; one or two squeezings of the bulb are generally sufficient.   No further attention is required until the precipitation is completed.   This completion may be ascertained by giving the precipitating flask a gentle shake.   If the pressure, as indicated by the manometer, does not show a momentary drop, the precipitation is complete.   When this has happened, close the screw clamp 8a, disconnect the safety flask, and the generator may be put aside until needed again. The rate of precipitation is often materially accelerated by giving the precipitating flask a gentle rotary motion every now and then.

The following precautions should be observed.   When the generator is under pressure, the screw clamp 8b must not be opened nor the precipitating flask disconnected, without first closing the screw clamp 8a.   The stoppers in the flask and generator must be securely inserted.   The screw clamp 8 must be closed after pumping the necessary air into the generator, and after precipitation is complete and the flask disconnected, it should be opened again before connecting the generator up for a precipitation. The opening of this screw clamp allows the pressure to return to atmospheric in the generator.

24. Digestion. — After precipitation, particularly of crystalline precipitates, the precipitate should be allowed to stand in contact with the supernatant solution for a sufficient length of time.   This procedure is necessary for two reasons: first, that the precipitation may have time to become quantitative; secondly, that the size of the initially fine crystals may grow so that they will be subsequently retained by the filter.   The time for quantitative precipitation·varies with the nature and amount of the precipitate; it seldom takes less than two hours and sometimes requires forty-eight hours (§ 186).   The increase in the size of crystals is hastened by increase of temperature, so that at elevated temperatures (60°–95°), two to three hours are usually enough time so far as the growth of the crystals is concerned.   To accomplish both of the foregoing desiderata without any real loss of time, it will be found a good practice to make precipitations late in the afternoon and allow the process of digestion to proceed overnight.[6]

[6] This assumes that the solution is not alkaline, as otherwise considerable carbon dioxide is likely to be absorbed from the air.

The phenomenon of digestion is interesting. Fine grained precipitates are known to have greater solubilities than coarse precipitates, consequently a solution which is saturated with respect to the fine particles in a precipitate will be supersaturated with respect to the coarse particles. This situation will bring about precipitation on the surfaces of the large particles, with the result that the small particles go into solution. The net effect of these changes is an increase in the particle size of the precipitate. An increase in particle size of a precipitate, since it is attended by a decrease in solubility, results in more complete precipitation. The relationship of particle size to solubility is shown by the data of Table 3, adapted from the results of Dundon.[7]

Table 3

EFFECT OF PARTICLE SIZE ON SOLUBILITY

Substance	Radius of Particle in Microns *	Per cent Increase in Solubility	Temperature °C
Ag_2CrO_4	0.3	10	26
PbF_2	0.3	9	25
CaF_2	0.3	18	30
$BaSO_4$	0.2	90	30

* 1 micron = 10^{-4} cm.

The per cent increase in solubility refers to the increase with respect to the solubility of the same precipitate when coarse crystals are in equilibrium with the solution.

After the precipitate has been formed and properly digested, it often becomes necessary to wash it free of impurities. This process of washing, as well as that of filtration, will be discussed in subsequent paragraphs. Some of the important pieces of apparatus made use of in these operations, namely the wash bottle, the policeman, and the stirring rod, as well as the desiccator, can be conveniently described at this juncture.

25. Wash Bottles. — A wash bottle is a flat-bottomed flask of convenient size, fitted up to deliver a fine stream of distilled

[7] Dundon, *J. Am. Chem. Soc.*, **45**, 2658 (1923).

water or other washing medium for the purpose of washing pre-
cipitates.   One wash bottle for use with water at ordinary
room temperatures will always be needed, and it is advisable
to have another for use when hot water (70°–90°) is needed; in
addition to these two wash bottles for water, it is well to provide
several smaller wash bottles for use with liquids other than
water.   Flat-bottomed flasks are invariably used, and the fol-
lowing sizes will be found convenient: for water, a flask of about
750-ml. capacity; for the other liquids, one of 500-ml. capacity.
The quality of the glass is very important as many kinds of glass
are appreciably soluble, particularly in hot
water.   Pyrex glass, however, is extremely
insoluble in water and is admirably suited
for wash bottles.   Figure 8 shows the general
arrangement of a wash bottle.
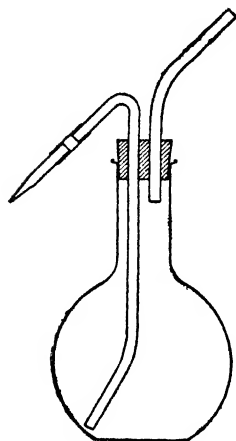
In the assemblage of a wash bottle the
following points are to be observed: the rub-
ber stopper (2-hole), when set firmly in place,
should project about half its length above
the top edge of the flask; if it projects more
than this it is likely to pop out when the
wash bottle is being used, while if less, it
will be troublesome to remove.   The mouth-
piece should be bent at an angle of 45°
and should just go through the stopper.
The lower end of the tube should extend
to the bottom of the flask and should
be curved forward as shown because this design allows of more
complete emptying of the contents of the wash bottle when
in use; the upper end of the tube should be bent at an angle
of 135° and in the same plane as the lower end; the top of the
bend should be about 3 cm. above the top of the cork and the
tube should extend about 4 cm. from the top of the bend.   It
is connected to the nozzle by means of a piece of soft rubber
tubing.   The nozzle should be about 4–5 cm. long and should
be drawn out to a taper, having an orifice of about 1 mm. diame-
ter.   This dimension can be arrived at by holding the tapered
end in a small flame and contracting the orifice by brief incipient

Fig. 8
Wash Bottle

melting until a size is reached that, upon trial, will deliver about 10 ml. of water in 10 seconds, when the full pressure of the breath is applied and maintained at the mouthpiece.

For hot water bottles, certain further points are to be observed. In order to protect the hand, the neck of the bottle should have fastened around it some suitable insulating material like sheet cork or asbestos paper, or a wrapping of heavy cord. The asbestos paper can be easily and satisfactorily applied as follows: Take a strip about 3 in. wide and 12–15 in. long and drench it with water; while it is still wet, wrap it snugly around the neck of the bottle and compress the several layers together by pressure of the hand; let dry overnight, and the bottle will be ready next morning. There is enough natural cement in asbestos paper to furnish its own binder. In order to protect the mouth from scalding by the back rush of steam through the mouthpiece when the pressure of the breath is removed, a three-hole rubber stopper should be used and a short piece of glass tubing, open at both ends, inserted in the extra hole. By keeping the thumb over this piece of tubing while the water is being blown out and then lifting the thumb before the blowing is stopped, there will be no back rush of steam into the mouth of the analyst. In the continuous use of a hot water bottle, the steam seems to disintegrate the rubber stopper so that small pieces of the stopper drop into the water and thus contaminate it, or else find their way through the outgoing stream of water into the precipitate being washed; consequently, the condition of the stopper should be frequently examined and a new stopper used when necessary.

26. "Policeman." — A "policeman" is an instrument which is used in connection with precipitates for the purpose of detaching from the walls of the containing vessel any adhering particles which it is not possible to remove by the stream of water from a wash bottle. Essentially, it is a stout piece of glass rod capped at one end with a piece of soft rubber tubing. The rod should be about 20 cm. long and should have a diameter between 5 and 7 mm.; the ends should be from 2–3 cm. long and should have a bore small enough to insure a tight fit over the glass rod; the end of the tubing should project about 2–3 mm. beyond the rod, as this makes a flexible annular ring which

adds greatly to the effectiveness of the "policeman." A police-
man should never be used in place of a stirring rod to pour
against, nor should it be left standing in solutions.

27. Stirring Rods. — Stirring rods are slender glass rods which
should be of assorted lengths with diameters about 4 mm. Both
ends should have their sharp edges gently fused in the gas flame
so that the rods will not cut the filter papers or scratch the
beakers. The proper length for a stirring rod is such that the
rod will not project more than 5 or 7 cm. beyond the lip of the
beaker in which it is used when it rests diagonally on the floor
of the beaker at a point directly opposite the lip. The student
should provide himself with six to twelve stirring rods.

28. Desiccator. — A desiccator is a vessel used for the purpose
of maintaining a dry atmosphere in which to place objects that

Fig. 9
Desiccator

might be affected by moisture or carbon
dioxide. The usual type (Figure 9) is pro-
vided with a ground-glass cover to keep it
air tight, and is designed so as to provide
a lower and an upper compartment. The
lower compartment is kept partially filled
with a suitable desiccating agent, such
as concentrated sulfuric acid or anhy-
drous calcium chloride. While the former
is slightly more efficient, in that it main-
tains a lower partial pressure of water va-
por, this efficiency is offset by the disad-
vantage that the acid is likely to splash around when the desic-
cator is being carried about. This splashing can be obviated
somewhat by filling the lower part of the desiccator with glass
beads. When anhydrous calcium chloride is used, it should
be granular and free from dust and should be renewed occa-
sionally. To obtain even dryer atmospheres than that obtained
with anhydrous calcium chloride, other desiccating agents can
be used, such as silica gel, anhydrous calcium sulfate or barium
oxide.
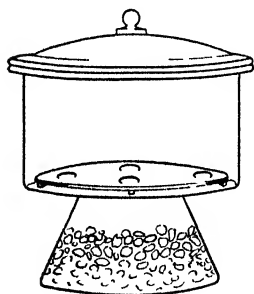
The upper compartment is fitted up particularly for the
accommodation of crucibles. For small desiccators, which as
a rule will take only one crucible, the fitting up is accom-

plished very satisfactorily by taking a silica or clay triangle with wire ends, and bending the ends so that they are perpendicular to the plane of the triangle, and then spreading them sufficiently so that their feet will press against the walls and floor of the compartment, thus preventing the triangle from sliding around. If the ends are too long, they can be cut off or bent back on themselves. Triangles of metal should never be used unless constructed of platinum. The ground-glass portions of the desiccator should be greased with a little vaseline so as to make the desiccator air tight.

When a hot object is placed in a desiccator, a sufficient time should elapse for the air to become heated and expanded before putting the cover in place, say 5–10 seconds; and when the cover is removed, it should be slid open very gradually to prevent any sudden inrush of air due to the partial vacuum which exists in the desiccator as a result of the previous escapement of hot air when the heated crucible was put in the desiccator. Failure to observe these precautions will often result in some of the precipitate being blown out of the crucible.

29. Filtration and Washing. — This operation is the separation of a precipitate from its supernatant solution, the object being to get the precipitate, and the filtering medium, quantitatively free from the solution and yet at the same time to prevent, as far as possible, any solution of the precipitate by the water or solutions used to wash away the adhering solution. Five devices used for filtration are: filter paper, the Gooch crucible, the Munroe crucible, the porous porcelain crucible, and the sintered glass crucible. With any of these the principle is always the same; it is in brief to so manipulate matters that, by the time we are ready to transfer the precipitate to the filtering device, a clean precipitate shall be put on a clean filter. To accomplish this end, resort is had to a procedure known as *washing by decantation.* The supernatant solution is carefully poured upon the filter,[8] a stirring rod being used to direct the stream of liquid as shown in Figure 10. Pouring is continued until the precipitate begins to flow along with it, when the pouring

[8] In pouring a solution upon a filter of any kind, the pouring should always be done against a stirring rod.

is stopped and the precipitate, with more or less supernatant solution, is allowed to stay in the containing vessel. A sufficient amount of washing solution is next poured into the vessel; the whole contents is stirred vigorously for a brief while, and the precipitate then allowed to settle, after which the new supernatant solution is decanted as before until the precipitate begins to run upon the filter. This process of treating with wash solution and following such treatment with decantation is repeated two or three times more; the filter is then washed directly with washing solution once or twice, after which the precipitate is transferred to the filter. In transferring a precipitate from a beaker or other vessel to a filter, the beaker is held in an inverted position with its lip or edge resting against a stirring rod while the bottom of the stirring rod rests on the filter. A fine stream of water from a wash bottle is played against the bottom and sides of the beaker as illustrated in Figure 11. This dislodges most of the precipitate which will be carried along with the water down the stirring rod and so be delivered upon the filter. Any precipitate that adheres to the walls of the beaker is detached by means of a "policeman," next rinsed into the bottom of the beaker by a fine stream of water, and then transferred to the filter in the manner just described.

Fig. 10
Transferring of Supernatant Solution to Filter

At this juncture, and before beginning the final washing of the precipitate on the filter, it is advisable to replace the beaker which has been receiving the filtrate by a fresh empty beaker. Frequently, when the final washing is begun, a little of the precipitate will run through the paper, and the precaution of changing beakers will save much time in case it is necessary to refilter. In the final washing of a precipitate on the filter, a

fine jet (see § 25) of wash solution should always be employed and the filter rinsed with this wash solution from its top edge down with enough diversion of the stream to stir up the precipitate thoroughly. When the filter is about three quarters full, the rinsing is stopped and the filter is allowed to drain until it is almost emptied of the solution; then the rinsing is repeated. In general, it will be found that it is useless to test for completeness of washing until the sixth rinsing; in some cases, it takes many more rinsings. In making the test for completeness of washing, it is usual to collect 1 or 2 ml. of the last drainings and test for some ion, known to have been present in the original supernatant solution. In a great number of cases, this will be chloride ion. It is always advisable to make tests of two successive drainings and compare them, as this will show the progress of the washing. It is also advisable to run a blank test upon the distilled water for chlorides, as it frequently happens that they will be found present. In general, it should be kept in mind that many small portions of wash water are much more efficient in removing impurities than a few large portions. See § 45, example 19.
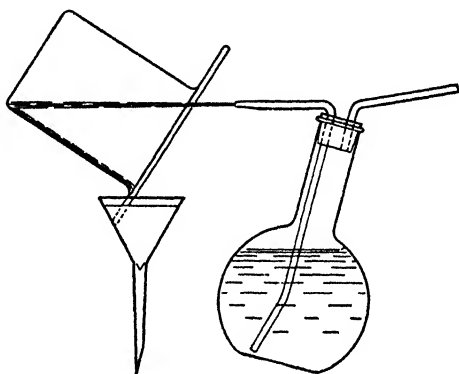
Fig. 11
Transferring of Precipitate to Filter

30. Filter Paper. — Filter papers for quantitative work should have a diameter of 11 or 12.5 cm., although, when the quantity of precipitate is small, papers having a diameter of 7 cm. are to be preferred. The ash of a quantitative filter paper of the size mentioned should not exceed 0.1 mg. In folding a filter paper to fit a funnel, it is extremely important that the paper should fit the funnel properly. In the first place the top of the paper should not be nearer the top of the funnel than 1 cm.; the carelessness of having a filter paper protrude beyond its funnel is unpardon-

[41]

able. In the second place the paper should rest smoothly against the walls of the funnel. A circular filter paper folded over on itself to form a semicircle of two leaves and this semicircle folded over again in such a way that the two edges do not exactly coincide, as shown in Figure 12, will form four leaves, two of which will have a slightly larger angle at the apex than the other two. If the filter paper is opened up by separating the two leaves having the larger angle, a solid angle will be formed which will be slightly larger than the solid angle of the funnel, of approximately 60°. When the filter paper is fitted into the funnel, the upper portion should rest completely against the walls of the funnel while the lower portion will not be in contact with the glass at all. By this method, the time of filtration can often be materially lessened. After the paper has been folded as described, it should be placed snugly in the funnel, moistened thoroughly with water, and the seams where the paper turns back on itself should be gently tamped down with the forefinger so that no precipitate can lodge in back of the fold. This is very important. The filter paper is now ready for use.

Fig. 12
Folding of Filter Paper

Filter papers are very convenient to use but offer the disadvantage that in the subsequent operation of ignition, the carbon resulting from the charring of the filter paper will reduce a greater or less fraction of certain precipitates. As examples, barium sulfate, silver chloride, and magnesium ammonium phosphate may be mentioned particularly. For gelatinous precipitates such as aluminum hydroxide or ferric hydroxide, filter papers are practically the only thing to use, as Gooch crucibles become clogged up almost immediately with precipitates of a gelatinous nature.

31. Macerated Filter Paper. — In the handling of gelatinous hydroxides, particularly those of the iron group, the use of macerated filter paper as suggested by Dittrich is to be highly recommended. Macerated filter paper is obtained by taking a quantitative filter paper — one with a diameter of 12 cm. is very con-

venient — tearing it into numerous small pieces, placing the pieces in a beaker and adding 10–20 ml. of 12 M hydrochloric acid. The acid is allowed to act upon the filter paper for 30 minutes or so until the pieces swell up considerably and then 100–200 ml. of water are added and the whole mixture is stirred. The result of this procedure is that the filter paper is disintegrated into thousands of small fibers. The macerated filter paper is now filtered on an ordinary filter paper and washed free of acid with water. After this, it is transferred to a bottle and 100 ml. of water added. It is now ready for immediate or future use. When wanted, it is shaken up with the water and added to the solution from which the hydroxides are to be precipitated, the addition not being made, however, until just prior to the precipitation. One 12 cm. filter paper furnishes just about the right amount of macerated filter paper for 200–300 mg. of hydroxides.

The macerated filter paper plays a rôle both in the washing and in the ignition of the precipitates. In the washing, it not only tends to prevent the characteristic cracking and channeling which gelatinous precipitates exhibit, but also enables the stream of wash solution from the wash bottle to stir the precipitate in a more efficient manner, with the net effect that the washing is accomplished in a much shorter time and with much less wash solution. In the ignition, it brings about the result that the precipitate, instead of being converted to a hard lumpy mass, crumbles away to a fine powder. This crumbling away continually presents new surfaces so that the time of ignitions is considerably shortened. Tablets of macerated filter paper can be purchased. They are made ready for use by shaking with water.

32. Gooch Crucible.[9]— A Gooch crucible is nothing more or less than a crucible which has its bottom perforated with numerous small holes, so as to form a skeleton framework for the support of a thin mat of asbestos fibers, the latter serving as

[9] F. A. Gooch, *Proc. Am. Acad. Arts Sci.*, **13**, 342 (1878). The original crucibles employed by Gooch were platinum, but subsequently the idea was extended to porcelain crucibles. Today, both platinum and porcelain crucibles go under the name of Gooch crucibles.

the filter medium.   The Gooch crucible is always employed with suction and the arrangement that is generally used with it is a stout-walled, side-necked Erlenmeyer flask of about 750 ml. capacity provided with a one-hole rubber stopper through which passes a funnel known as a Gooch funnel. The top of the funnel is capped with a piece of rubber tubing to serve as a gasket for the support of the crucible.   The general arrangement is shown in Figure 13.

In the use of a Gooch crucible it is important that the bottom of the crucible be far enough below the rubber gasket so that the filtrate will not come in contact with the rubber.   There are several ways of attaching the rubber tubing to the funnel, but the authors have found the following method to be the best as it provides a gasket which not only makes an air-tight seal but, at the same time, provides an air cushion for the crucible and prevents its binding in the funnel.   The rubber tubing should be about 7 cm. long and 4 cm. wide; it is first put on the funnel as shown in Figure 14 (position 1); it is next folded back on itself (position 2); the outer layer of rubber is then worked down over the inner layer with the fingers until the opening for the crucible is just a little less than that of the funnel itself (position 3).

Fig. 13
Arrangement for
Gooch Crucible

In preparing the asbestos mat, some short fiber asbestos (about 0.5 cm.), which has been washed in acid and ignited, is suspended in water and let stand for a short time to allow the asbestos to settle.   The top portion of the water is discarded, after which enough of the asbestos pulp is allowed to flow upon the crucible, which is under slight suction in the set-up just described, until the mat will have a thickness of 1–2 mm. when spread out evenly.   A mat of this thickness will be slightly translucent when held up to the light.   The suction is now broken by slipping off the rubber connection from the side-neck Erlenmeyer flask, the crucible is filled with distilled

water, and the asbestos is stirred up with a stirring rod; suction
is then applied and the mat is sucked down tight; this pro-
cedure is repeated three or four times in order to get rid of
very short fibers and any soluble matter.   The crucible is
now placed over a very small Bunsen flame for a few minutes
to drive off any water; the flame is then gradually increased
and the crucible strongly ignited for 5–10 minutes.   After
being allowed to cool in the desiccator, it is placed in the
filter funnel and washed with about 200–300 ml. of distilled
water.   It is ignited a second time, allowed to cool in the
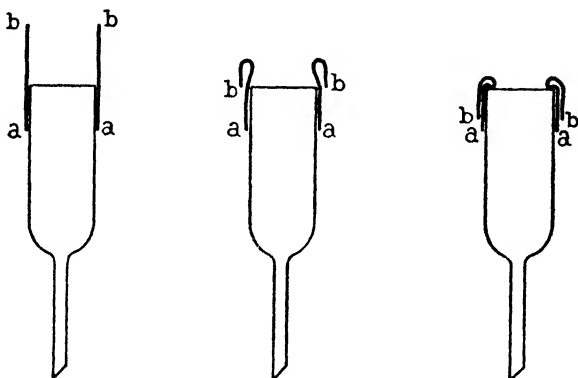
Fig. 14

Manner of Fitting Rubber Tubing to Gooch Funnel

desiccator and weighed.   The crucible should not be handled
with the fingers from this point until after the final weighing is
made, but should be lifted by means of a pair of crucible
tongs.   The crucible is next washed with the same quantity of
water as before, ignited, allowed to cool, and weighed a second
time.   The two weighings should agree within 0.1 mg. for
platinum Gooches and 0.2 mg. for porcelain Gooches.   If they
do not, successive washings, ignitions, and weighings are made
until this concordance is attained.   The great advantage of
igniting the asbestos mat is not only that it brings about a
much finer inter-meshing of the fibers, thus allowing the fil-
tration of the finer-grained precipitates, but it also reduces the

number of treatments necessary to bring the crucible to constant weight.

An asbestos mat, made from a good grade of asbestos fiber, does not seem to be affected when treated by acid solutions up to one molar or by alkaline solutions (which are not too strongly alkaline) such as ammonium hydroxide or dilute alkaline carbonate solutions. The practice of using a Gooch crucible for more than one determination is not to be recommended; a fresh Gooch should be prepared for each determination.

33. Munroe Crucible.[10] — A Munroe crucible is really a modified Gooch crucible in which the filter medium, instead of being made of asbestos fibers, is an extremely thin layer of porous platinum deposited on the bottom of the Gooch crucible. Munroe crucibles are always of platinum, whereas Gooch crucibles may be either of platinum or porcelain. The advantages of the Munroe crucible are its rapidity of filtration; retention of the finest precipitates, such as calcium oxalate, barium sulfate, etc.; its almost complete insolubility in fairly concentrated acids and alkalies; and its requirement of almost no previous treatment to get it ready for a filtration.

Preparation of a Munroe Crucible.—According to the results obtained by Snelling,[11] who made an extended investigation of the method for preparing a Munroe crucible, a concentrated solution of chlorplatinic acid containing the equivalent of 0.450 g. platinum is precipitated by a solution of ammonium chloride and the resulting ammonium chlorplatinate washed several times by decantation with water and then with alcohol. A perforated platinum crucible is now placed upon several layers of filter paper and held firmly in this position while the alcohol-moist precipitate of ammonium chlorplatinate is poured into it so as to form a uniformly distributed layer of from 0.25 to 0.50 cm. thickness. As soon as the alcohol has been absorbed by the filter paper, the crucible is dried in a water or electric oven at about 100° until the alcohol has been entirely

[10] C. E. Munroe, *J. Anal. Chem.* **2**, 241 (1888); also *Chem. News*, **58**, 101 (1888).
[11] W. O. Snelling, *J. Am. Chem. Soc.*, **31**, 456 (1909).

driven off, after which the crucible is gently heated over a Bunsen burner until the decomposition of the ammonium chlorplatinate has been effected, the heating then being continued and increased until the crucible reaches dull redness. The salt should be shaped during ignition, while after ignition the layer of coherent platinum sponge which has been formed should be gently burnished with a glass rod flattened somewhat at the end. If the mat retains cold, freshly-precipitated calcium oxalate, it may be considered free from cracks and sufficiently fine to hold the finest precipitates.

In case cracks or imperfections have developed in the mat or subsequently develop from any cause,[12] the crucible may readily be restored to prime condition by saturating it with concentrated chlorplatinic acid solution and then allowing a moderately strong, aqueous solution of ammonium chloride to diffuse upwards throughout the mat by lowering the crucible slowly into a beaker containing the ammonium chloride solution, washing with alcohol, drying and igniting.

Cleaning a Munroe crucible.[13]— In many instances in the cleaning of a Munroe crucible, a part, at least, of the precipitate may be shaken or gently blown out, but the mat can be completely cleansed only by the aid of solvents; this method of procedure is an essential feature of the use of the Munroe crucible. It is to be noted that hot, concentrated sulfuric acid and hot hydrochloric acid, if used alone, cause a decided loss of the mat, the former by rendering the finely divided platinum colloidal, in which condition it is readily carried through by the wash water, the latter by taking up the platinum as chloride. However, both these acids may be used freely in the crucible without causing the slightest weighable loss of platinum, provided that ammonium salts, alkali or ammonium nitrates, or nitric acid are added to the sulfuric acid, while ammonium salts other than the nitrate are added to the hydrochloric acid. Besides the solvents just mentioned, Swett describes about forty others, the complete list of which must be sought in the original article.

[12] This paragraph drawn almost verbatim from the article of O. D. Swett, *J. Am. Chem. Soc.*, **31**, 932 (1909).
[13] *Ibid.*

The partial list given in Table 4 includes such precipitates as are likely to be ordinarily encountered; the reference numbers show the proper solvent to be used with a given precipitate:

Table 4

LIST OF SOLVENTS

(Salts are applied in aqueous solution unless otherwise specified.)

1. Water
4. Sulfuric acid with nitric acid or nitrates
5. Sulfuric acid, concentrated or fuming with ammonium chloride
6. Nitric acid
10. Hydrochloric acid with ammonium chloride or oxalic acid

12. Potassium hydroxide
13. Sodium hydroxide
14. Ammonium hydroxide
15. Potassium sulfide
19. Ammonium sulfide
22. Sodium thiosulfate
27. Ammonium acetate (alkaline)
36. Ammonium chloride

CHOICE OF SOLVENT FOR A GIVEN PRECIPITATE

(Numbers indicate correspondingly numbered solvents in the preceding list. Hyphens indicate successive treatments, commas indicate alternative treatments. Abbreviations: h = hot, c = concentrated, d = dilute)

ammonium magnesium arsenate	6, 10
ammonium phospho-molybdate	1h, 12, 13, 25, 26, 29, 30, 36
antimony trisulfide	10c, 12d, 15, 19
barium chromate	6, 10
barium sulfate	4h, 5h
calcium carbonate	6d, 10d
calcium carbonate ignited	1h, 6d, 10d
calcium fluoride	4, 10c
calcium oxalate	6, 22
lead chromate	6, 12
magnesium pyroarsenate	6, 10
magnesium pyrophosphate	6, 8, 10, 6ch, 10ch
manganese dioxide	10h
metastannic acid	10, 13
potassium chlorplatinate	1h, 12h
silver chloride	14h
stannic oxide	36 dry-ignition, 10-1
zinc oxide	10dh
zinc sulfide	4, 6, 10

34. Porous Porcelain Crucibles. — A porous porcelain crucible, made of glazed porcelain walls and a porous porcelain bottom, makes a very convenient filter. Suction, applied in the same way as with the Gooch crucible (Figure 13), causes the filtrate to pass through the porous bottom. The precipitate, however, is retained in the crucible. These crucibles can withstand high temperatures provided they are not heated or cooled too rapidly. The heating should be carried out in a furnace or in a porcelain crucible if a gas flame is to be used. Precipitates in this type of crucible can be dried by first applying suction to remove as much water as possible and then either drying to constant weight in a beaker placed inside of a constant temperature oven, or in a porcelain crucible placed in a muffle furnace, or heated by a gas flame.

35. Sintered Glass Crucibles. — A sintered glass crucible is made of glass walls and porous, sintered glass bottom. Filtration is carried out with these in the same manner as with the porous porcelain type. In applying heat, care must be taken not to change the temperature too rapidly. It is inadvisable to heat these crucibles above 600°.

36. Silver Nitrate Test Bottle. — The silver nitrate test bottle is used for containing a solution of silver nitrate fairly acid with nitric acid. The purpose of the solution is to test wash waters for evidence as to whether a precipitate has been completely washed or not. It is assumed in the washing of precipitates that the washing is completely accomplished and all soluble substances quantitatively removed when any particular substance, originally present in the solution from which precipitation was made, is quantitatively removed. Since in the great majority of cases precipitation is made from solutions containing chlorides, and the silver chloride test is a very delicate and satisfactory one, it follows that this test is the one that is most usually made.

The silver nitrate, nitric acid solution should be kept in a 100 ml. amber-colored bottle. A cork stopper, projecting about half its length above the top edge of the bottle, should be employed and should be bored so as to accommodate a glass tube about 6 mm. in diameter. This tube should extend nearly to the bottom of the bottle and should project about 7 cm.

above the top of the cork; its lower end should be drawn out somewhat so as to facilitate the formation of drops, while the upper end should have its sharp edges rounded by holding in the gas flame for a while; a small plug of cotton wool should be placed in the upper end of the tube to prevent dust from getting into the bottle. The cork should not be jammed into the mouth of the bottle but should rest gently so that it can be lifted out with one hand.

37. Ignition. — In igniting precipitates, it was formerly the practice to dry the filter paper together with the precipitate in an oven (usually at 100°–105°), then to detach as much of the precipitate as possible from the filter paper and to ignite the latter separately, after which the main portion of the precipitate was added to the crucible and the ignition completed. Instead of following this procedure, it is now customary, except when carbon from charred filter paper will reduce the precipitate (see § 30 and § 204) to transfer the moist filter paper and precipitate directly to the crucible and to conduct the ignition by first gently heating the crucible (with its cover on to prevent access of air) until all the water is driven off and the filter paper is gradually and completely charred. During this stage of the ignition, the crucible is maintained in a vertical position. After the carbonization has been effected, the cover is removed so as to allow free access of air. The crucible is next placed in an inclined position on the triangle and the full flame of the burner employed, while, every 10 minutes or so, the crucible is turned slightly by means of the tongs so as to expose fresh portions of the precipitate. Usually it takes about 20 minutes to char the paper and about 30 to 40 minutes more to complete the ignition. The crucible and ignited precipitate are placed in a desiccator, allowed to cool, and weighed. The precipitate is then ignited a second time for the same period as in the first ignition, then cooled and weighed. The two weighings should agree within 0.2 mg. if a porcelain crucible has been employed; if a platinum crucible has been used, then the concordance of the weighings should be within 0.1 mg., provided that temperatures above 1,000° have not been used. If temperatures above 1,000° have been used, allowance must be

made for the change in weight of the crucible due to the volatility of platinum above 1,000°. (See § 89.)

The practice of using covered crucibles is to be recommended. When a hot crucible is placed in a desiccator, part of the air is driven out of the desiccator, so that, upon cooling, a partial vacuum is created. When the cover of the desiccator is removed in order to take out the crucible, a sudden inrush of air results and this will frequently blow some of the precipitate out of the crucible if the latter is not covered.

38. Drying. — As already mentioned in Chapter I, it is customary in the case of many substances, such as minerals, soils, clays, salts, etc., to report analyses on what is known as the *moisture-free basis*. For this purpose it is necessary to make a determination of the moisture in the sample. Instead, however, of actually isolating the water and weighing it, it is a more general practice to dry the sample at some arbitrary temperature between 100° and 110° until constant weight has been attained, and then regard the loss in weight as representing the moisture originally present. This determination of loss in weight should always be made on a separate portion of the sample, as other changes in the composition of the sample may occur during the process, particularly if the sample contains a substance which is easily oxidizable. The procedure is to take a platinum *milk dish*, or, lacking this, a platinum or porcelain crucible, and to heat it in the flame of the Bunsen burner for 5–10 minutes, to allow it to cool in the desiccator and to weigh it. Two grams of sample are then placed in the dish or the crucible, after which the dish or the crucible, along with its contents, is placed in a constant-temperature oven or air bath, and allowed to remain there for several hours, when it is withdrawn, cooled, and weighed. The heating is again continued for another interval, another weighing made, and so on until constant weight is attained. The percentage of moisture is always figured on the original weight of sample, and, in stating the result found, the temperature of drying should always be mentioned. An illustration of a calculation in which the per cent of moisture in a sample is made use of in calculating the per cent of copper in a sample of copper ore is given in § 5.

39. Constant Temperature Oven. — In quantitative analytical work a constant temperature oven is almost indispensable. Electrically heated, thermostatically controlled ovens are to be preferred. Figure 15 shows an oven of this type.
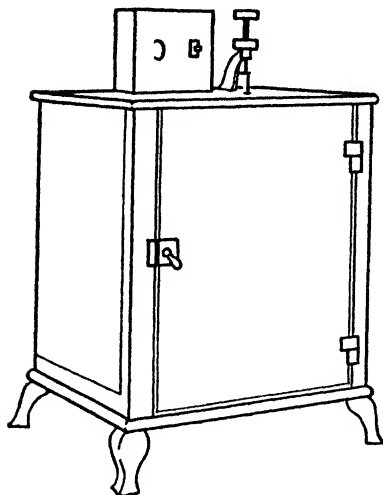
40. Reagents. — In carrying out a quantitative analysis the analyst is confronted with the danger of introducing impurities which may effect his results. Such impurities may be found with the reagents used and hence the proper selection and storage of reagents should receive careful consideration.

Purity of Reagents. — It cannot be emphasized too strongly that the analyst should always take the greatest pains to make certain of the purity of his reagents. To this end, he should always employ only the best grades of "analyzed chemicals."[14] Even then, he should not accept the published analysis on the label as his final authority but should check up matters by running a blank test for any impurity, whether it is listed or not, which would interfere in the analysis to be performed.[15]

Fig. 15
Constant Temperature Oven

While the "analyzed chemicals" which are now obtainable for quantitative work mark a distinct advance over those merely

[14] Am. Chem. Soc. Committee on Guaranteed Reagents, *Ind. Eng. Chem.*, **17**, 756 (1925); **18**, 636, 759 (1926); **19**, 645, 1369 (1927); **20**, 979 (1928); *Ind. Eng. Chem. Anal. Ed.*, **1**, 171 (1929); **2**, 351 (1930); **3**, 221 (1931); **4**, 154, 347 (1932); **5**, 289 (1933).

[15] For the testing of chemical reagents, the student is referred to the admirable work of C. Krauch, "Chemical Reagents, Their Uses, Methods of Testing for Purity and Commercial Varieties," 2nd English Edition, Revised and Enlarged by H. B. Stocks, Scott Greenwood & Son, London, 1919.

For methods dealing with the preparation of pure reagents for analytical purposes there does not seem to be any single collected work although there are

labeled "C.P." in that the impurities are not only stated on the label but their percentages given, it must always be borne in mind that a label is by no means an infallible criterion. There are several reasons for making this assertion. In the original unopened bottle, certain impurities might not have been tested for by the manufacturer, while very often dust and stray pieces of straw or cork will be present in spite of the greatest care used in packing; in bottles which have been opened, there is always a chance that some one may have left the bottle uncorked for a time with consequent contamination of the contents from the fumes of the laboratory, or else an unused portion of the reagent may have unwittingly been returned to the package, or, through gross mistake, may even have been put in a wrong package. In packages which have been dispensed from others there are, in addition to the foregoing chances of impurity, the ones that a false label may have been applied or that the new package might not have been thoroughly clean. It must further be remembered that alkaline solutions that are kept for any length of time in glass containers will be contaminated with soluble constituents from the glass.

41. Concentrations of Reagents. — There are several ways in use for designating the concentration of a reagent, and these are discussed in detail in Chapter VIII. The system that we shall use now and throughout our work will be the molar system. The units of this scheme are the mole and the liter; a mole being the formula weight in grams of a substance; a molar solution being one which contains one mole of reagent per liter of solution. Thus a molar solution of silver nitrate (mol. wt. 169.9) is one which contains 169.9 g. silver nitrate per liter of solution; a tenth-molar solution of hydrochloric acid (mol. wt. 36.46) is one which contains 3.646 g. HCl per liter of solution. The symbol M is used for molar, whence it follows that the concentration of

several books on preparation of inorganic salts, particularly by L. Vanino, "Handbuch der Präparativen Chemie, Band I, Anorganische Teil," Ferd. Enke, Stuttgart, 1925. Also Biltz, Hall and Blanchard, "Laboratory Methods of Inorganic Chemistry," 2nd ed., John Wiley & Sons, New York, 1928. In the main, it is mostly a question of searching the literature for articles dealing with the particular reagent in question.

a solution designated as 5 M would contain 5 moles of a substance per liter of solution; and one marked 0.2 M would indicate a concentration of two-tenths of a mole of substance per liter of solution.   For general analytical purposes the following concentrations of reagents are those commonly employed; the concentration, however, need only be approximate:

Acid Acetic 17 M: Concentrated acetic acid, sp. gr. 1.064, containing about 96% CH_3COOH

Acid Citric 0.2 M: 42 g. $(CH_2 \cdot COOH)_2 C(OH)(COOH) \cdot H_2O$ made up to 1 liter

Acid Formic 24 M: Concentrated formic acid, sp. gr. 1.205

Acid Hydrochloric 12 M: Concentrated HCl, sp. gr. 1.19–1.20 and containing about 39–40% HCl by weight

Acid Hydrochloric 3 M: Made by dilution of the 12 M HCl

Acid Nitric 16 M: Concentrated nitric acid, sp. gr. 1.42 and containing about 69% HNO_3 by weight

Acid Sulfuric 18 M: Concentrated sulfuric acid, sp. gr. 1.84 and containing about 97% H_2SO_4 by weight

Ammonium Chloride 3 M: Made by dissolving 160.5 g. of NH_4Cl and diluting to 1 liter

Ammonium Hydroxide 15 M: Concentrated NH_4OH, sp. gr. 0.90 and containing about 28% NH_3 by weight

Ammonium Hydroxide 3 M: Made by dilution of 15 M NH_4OH

Ammonium Oxalate 0.25 M: This is practically given by a saturated solution at 20–25°

Barium Chloride 0.1 M: Made by dissolving 24.4 g. of $BaCl_2 \cdot 2H_2O$ and diluting to 1 liter

Potassium Sulfocyanate 0.1 M: Made by dissolving 9.7 g. KCNS and diluting to 1 liter

Di-Sodium Hydrogen Phosphate 0.25 M: Made by dissolving 89.5 g. $Na_2HPO_4 \cdot 12H_2O$ and diluting to 1 liter

42. Reagent Bottles. — Every reagent bottle should always be kept scrupulously clean, particularly around the neck and mouth; a good plan is to have at hand a small, dampened, clean cloth and to wipe these parts carefully prior to using the reagent. The stopper should never be laid upon the desk, but should be held between the fingers or placed upon a clean watch glass; and it should be returned immediately to its bottle as soon as the

reagent has been withdrawn. All glass seems to be attacked more or less rapidly by the solvent action of solutions, particularly by alkaline solutions, and it is important to select the most resistant glass possible. One of the best glasses for this purpose is the boro-silicate glass put out by the firm of Whithall-Tatum Co., New York, N. Y., under the trade name of "Non-Sol."

43. Distilled Water. — Distilled water should be used in all analytical work, and in certain cases where the ordinary distilled water is not sufficiently pure, specially prepared distilled water (conductivity water) must be used. As generally prepared by boiling tap water and condensing the steam, distilled water is purified to the extent that most of the non-volatile constituents ($NaCl$, $CaCO_3$, $MgSO_4$, etc.) are left behind, but, on the other hand, the volatile constituents, originally present in the water (*i.e.*, ammonia, carbon dioxide) or generated during the distillation by the decomposition of the organic compounds or micro-organisms present (*i.e.*, ammonia, volatile fatty acids, etc.), will be found to have passed over and to be contained in the distillate. If the steam is condensed by means of a glass condenser, there will be a further contamination of the distillate due to the fact that steam has a marked solvent action upon glass. The best condenser to use is one made of pure block tin. It is hard to set any figures as to the amount of impurities in distilled water of one distillation because the amounts of impurities depend largely upon the source of the tap water, the material of the condensing tube,

Table 5

A SAMPLE OF NEW YORK CITY WATER

	Original Water Milligrams per Liter	After Distillation from Continuous Still Milligrams per Liter
Chloride..............	8.4	not determined
Ammonia.............	.1	0.6
Carbon dioxide........	8.0	6.0
Loss upon ignition.....	21.0	5.0
Fixed solids...........	41.0	8.0
Iron.................	.5	—

and somewhat upon the rate of distillation. In any event, distilled water is far from being absolutely pure water. The figures

given in Table 5 may perhaps be taken as indicative of what we may expect for distilled water prepared by the single distillation of a good potable water; the figures give the analysis of a sample of distilled water resulting from one distillation of New York City tap water from a continuous iron still with a block tin condenser; by way of comparison the impurities in the original tap water are given.

44. Conductivity Water. — This is a name applied to distilled water of a very high degree of purity. For the preparation of conductivity water there are available several methods which
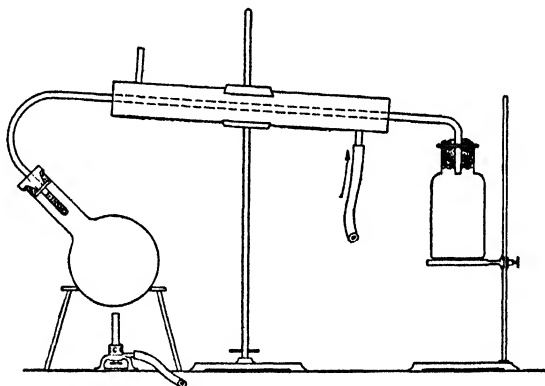
Fig. 16
Still for Conductivity Water

are more or less elaborate, depending on the desired purity of the water; for the details of these the student is referred to the original articles.[16] The following method, while not giving conductivity water of the utmost purity, is very satisfactory for many purposes and moreover is quite simple.

One to two liters of distilled water are placed in a large round-bottomed flask having a capacity about twice the volume of water used. The flask is connected to a block tin condenser by means of a one-hole block tin stopper which is tapered and flanged at the top and bottom so that it can be wrapped with asbestos cord to serve as a packing. It is advisable to fit a small

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[16] Bourdillon, *J. Am. Chem. Soc.*, **103**, 791 (1913); Kraus & Dexter, *ibid.*, **44**, 2468 (1922).

spray trap into the stopper. The trap is easily made by taking a piece of block tin tubing about 3 in. long, closing one end but providing the other end with a thread so that it can be screwed into the stopper, and then drilling the walls with numerous tiny holes. The general arrangement is portrayed in Figure 16.

After the water has been placed in the flask, a handful of glass beads is added to prevent subsequent bumping, then 50 ml. of alkaline potassium permanganate solution containing 8 g. potassium permanganate and 300 g. potassium hydroxide per liter,[17] and the distillation is started. Affairs are now so adjusted that about 4 ml. of water are condensed per minute while at the same time a small amount of steam is escaping at the exit end of the condenser. The first 300 ml. of the condensate are rejected as this will contain ammonia; the succeeding portions of condensate are collected, until about one-quarter of the original water remains in the distilling flask; then the distillation is stopped. Conductivity water rapidly becomes contaminated when stored in even the better grades of non-sol glass, so that only enough water should be prepared to take care of immediate needs.

The figures given in Table 6 show the quality of conductivity water prepared by this method, starting with the distilled water mentioned in § 43 and resorting to only one distillation from alkaline permanganate.

Table 6

SAMPLE OF CONDUCTIVITY WATER

	Milligrams per Liter
Chloride....................	none
Ammonia	0.03
Carbon dioxide..............	2.0
Loss upon ignition...........	1.2
Fixed solids.................	4.0
Conductivity	1.0×10^{-6} reciprocal ohms
Concentration of hydrogen ion (by p-nitrophenol)..........	$10^{-5.3}$

[17] The function of the alkaline permanganate is to decompose the nitrogenous and other organic substances (acids) present in the water.

45. Examples.

1. Calculate the number of grams of solute required to make each of the following solutions:

(a) 500 ml. of 0.1 M $AgNO_3$
(b) 200 ml. of 0.1 M K_2CrO_4
(c) 200 ml. of 0.05 M $BaCl_2 \cdot 2H_2O$
(d) 1,000 ml. of 0.05 M $K_4Fe(CN)_6 \cdot 3H_2O$
(e) 1,000 ml. of 0.1 M $Na_2S_2O_3 \cdot 5H_2O$

2. Calculate the approximate volume of concentrated acid required to make the following solutions:

(a) 1,000 ml. 0.1 M HCl made by diluting 12 M HCl
(b) 200 ml. 0.1 M HNO_3 made by diluting 16 M HNO_3

3. Calculate the weight of $KMnO_4$ required to make 1,000 ml. of 0.02 M solution. Assume that 0.04 g. of $KMnO_4$ are decomposed in the process of making up the solution.

4. Calculate the quantities required to make up 100 ml. of molar concentration of the following substances: KCl, Na_2CO_3 and $FeCl_3$.
                    Ans. KCl = 7.46 g., Na_2CO_3 = 10.59 g., $FeCl_3$ = 16.22 g.

5. If each of the above solutions were diluted to 500 ml., what would be their respective molarities?   Ans. 0.2 M

6. If 1,000 ml. of copper sulfate solution were made by using 53.46 g. of $CuSO_4 \cdot 5H_2O$, what would be the molarity of such a solution?
                                                                Ans. 0.214 M

7. How many milliliters of 18 M H_2SO_4 are required so that, when diluted to a liter, 5 ml. will contain 0.49 g. of H_2SO_4?   Ans. 55.5 ml.

8. In 74 ml. of solution of a certain salt, the molarity of which is 4.5, the salt content is 19.48 g.   What is the formula weight of the salt?
                                                                Ans. 58.4 g.

9. What is the molarity of a potassium permanganate solution of which 35 ml. contain 0.770 g. $KMnO_4$?   Ans. 0.14 M

10. An analyst added 10 ml. of 0.1 M silver nitrate solution to 15 ml. of dilute hydrochloric acid, diluted with 200 ml. of water, and obtained a precipitate of AgCl which weighed 0.0716 g. (complete precipitation assumed). What was the molarity of the hydrochloric acid? Ans. 0.033 M

11. In an analytical method for the separation of the Iron and Rare Earth Groups from manganese, nickel and magnesium, it is prescribed that a solution of ammonium chloride be used, the concentration of which is 5 g. of NH_4Cl in 200 ml. of solution.   What is the molarity of this solution?   Ans. 0.47 M

12. In the determination of ferric iron, according to Knecht and Hibbert, a titanous chloride solution is used, the strength of which is 1 per cent TiCl$_3$. If the density of the solution at 20° were 1.005, what would be the molarity?   Ans.   0.065 M

13. As a means of effecting the solution of a Type Metal alloy, it is recommended to use 15 ml. of 12 M hydrochloric acid to a gram of sample, as the first step in the analytical procedure. How many grams of hydrogen chloride are contained in this amount of hydrochloric acid?
                                                        Ans.   6.57 g.

14. The specific gravity of a certain sulfuric acid solution at 15°–15° is 1.810 and its percentage content of H$_2$SO$_4$ is 88.5%. How many milliliters of the acid must be diluted to 1 liter in order to give a resulting solution which shall be 6.0 M?   Ans.   367 ml.

15. A carload of soft coal weighing approximately 60,000 lbs. is to be sampled for analysis. The pieces range in size from $\frac{1}{4}$ mesh to 12″ dia. Describe how you would proceed with the sampling.

16. A quantity of boiler water (50 gal.) containing considerable sediment is to be sampled. Describe how you would proceed.

17. A liter of 9 M nitric acid is required. How many milliliters of nitric acid of sp. gr. 1.40 must be diluted to 1 liter to furnish this?

18. What would be the surface of 0.200 g. of hematite iron ore (density = 5.0) if ground to (a) 10 mesh, (b) 100 mesh? Assume the particles to have an equivalent diameter equal to the mesh opening.

19. In the washing of precipitates, let us suppose that a precipitate is placed upon a filter paper; let C_0 represent the concentration of the mother liquid which is to be washed from the precipitate, v the volume of the liquid which remains behind after the precipitate has drained, and v_1 the volume of the liquid poured on the precipitate. Then it can be shown that the residual liquid which remains after the nth washing is

$$vC_n = \left(\frac{v}{v+v_1}\right)^n vC_0.$$

Show that if the amount of liquid poured on the precipitate at each washing is nine times the amount of residual liquid retained by the precipitate, then, after the fourth washing the concentration of the mother liquid will be 1/10,000th of its original value (J. W. Mellor, 1898).

20. Calculate the surface of 0.200 g. BaSO$_4$ (density 4.4) if the particle size is such that the equivalent diameters are of the order of 10^{-7} cm.

CHAPTER III

PRECISION

46. Frequent Occurrence of Error in Quantitative Measurements. — Before undertaking his laboratory work, the student will find it very profitable to become acquainted with the general principles of precision,[1] not only in order to know how carefully he should make his measurements, but also to know to what extent he can rely upon his results.

It has perhaps been too generally taken for granted that quantitative methods are on a thoroughly satisfactory basis, and that, as a consequence, the student has only to run duplicate determinations until exact checks are obtained in order to insure accuracy. Such an idea is very harmful because it implies that determinations are free from all errors except those arising from some fault of the student. Thus the student misses the essential point that, besides his own mistakes, there are also the errors which lurk in every experimental method even when conducted with the most extreme care. It must be continually borne in mind that every determination is an approximation which is attended with more or less error and that in no case is it possible to reduce the error to zero.

47. Precision. — By the precision of a series of measurements we mean the narrowness of the limits within which the observed values lie. The narrower these limits, the better the precision is considered to be. The methods of obtaining an

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[1] The following notes on precision are intended to be only such a brief treatment of the subject as will be of interest to the student of analytical chemistry. For a comprehensive treatment of the subject of precision, the reader is referred to any of the following works: H. M. Goodwin, "Elements of the Precision of Measurements and Graphical Methods," 2nd ed., McGraw-Hill Book Company, Inc., New York, 1920. L. D. Weld, "Theory of Errors and Least Squares," The Macmillan Co., New York, 1916. T. W. Wright and J. F. Hayford, "Adjustment of Observations by Least Squares," 2nd ed., D. Van Nostrand Co., New York, 1906.

estimate of these limits will be discussed in later paragraphs of this chapter. It should be pointed out here that the term *accuracy* is often used carelessly in place of the term *precision* in connection with the results of physical or chemical measurements. By accuracy of a result would be meant the concordance between it and the true value of the quantity measured. This concordance, however, is impossible to ascertain because the true value of any physical quantity is unobtainable. The value we get as a result of our measurements, after correcting for all known sources of error, is only a more or less close approximation to the true value. Hence, to employ proper terms, we must speak of the precision of a measured result and not of its accuracy.

The allowable limits of error in a given determination must be known if we are to determine whether or not our results possess the necessary degree of precision. To deal with this question, we notice that the final values which are set down for the results of determinations are derived measurements in that they are obtained by means of calculation from one or more directly measured quantities. Consequently, the final values will be affected by the errors in the primary measurements, or, in other words, the ultimate error with which we are concerned in any given determination is a function of the errors which exist in the primary measurements.

Let us now discuss the general nature of errors, and then later show the effect which errors in the primary measurements have upon the final result.

48. Classification of Errors. — When any quantity is measured to the full precision of which the instrument or method employed is capable, it will, in general, be found that the results of repeated measurements do not exactly agree. This is true not only of results obtained by different observers using different instruments and methods, but also of results obtained by the same observer under similar conditions. The cause of these discrepancies lies in various sources of error to which all experimental data are subject. When we examine the nature of these sources, we find that, for our purpose, errors may be conveniently grouped into two classes:

     1. Accidental
     2. Systematic

49. Accidental Errors. — Accidental errors are those errors which manifest themselves by the slight variations that occur in the case of successive observations made by the same observer under as nearly identical conditions as possible. They are due to causes over which the observer has no control and which, in general, are so intangible as to be incapable of analysis, as, for example, slight differences in the judgment of the observer, or in the behavior of the instruments, or in the relative amounts of the substances which have reacted, as we proceed from one determination to another.

It has been shown that the magnitude and sign of errors of this kind follow a perfectly definite law, namely, the *Law of Chance*, the equation for which is [2]

$$y = \frac{h}{\sqrt{\pi}} e^{-h^2 x^2}$$

where y is the frequency of the occurrence of an error of the magnitude x, h is a constant, the value of which depends upon
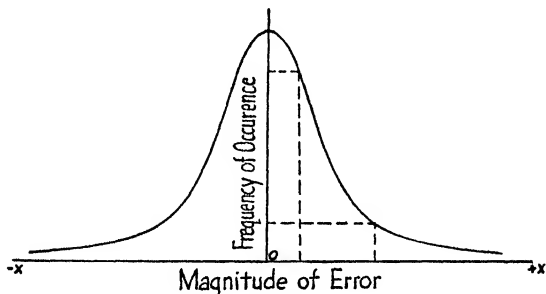
Fig. 17

Probability Curve

the character of the observations and which affords a measure of their precision, and e is the base of the natural system of logarithms and has the numerical value, 2.718. The curve represented by this equation, and shown in Figure 17, is called the

[2] This equation is due to Gauss. See "Theoria Motus Corporum Coelestium," Lib. II, Sec. III, Art. 178 (1809); also "Bestimmung der Genauigkeit der Beobachtung," *Z. Astrophys.*, 1816.

Curve of Error or the Probability Curve. An inspection of this curve shows that:

1. Small errors occur more frequently than large ones.
2. Very large errors are unlikely to occur.
3. Positive and negative errors of the same numerical magnitude are equally likely to occur.

The generalization that positive and negative accidental errors of the same numerical magnitude are equally probable represents a limiting case corresponding to a very great number of observations. Deductions from it with respect to a small number of observations apply less rigidly, the fewer the number of observations.

This generalization, that positive and negative accidental errors of the same numerical magnitude are equally probable, leads to the conclusion that the best value to select for a series of equally trustworthy observed readings which follow the Law of Chance is such a value that the differences between the observed readings and it shall balance each other. This value we find to be the *Arithmetical Mean*.

It is easy to verify this choice of the arithmetical mean. Let the several measured results be designated by a_1, a_2 . . . a_n and their arithmetical mean by m. Then

$$a_1 - m = d_1$$
$$a_2 - m = d_2$$
$$a_n - m = d_n$$

Adding these, we obtain:

$$(a_1 + a_2 + \ldots + a_n) - nm = (d_1 + d_2 + \ldots + d_n) \quad (1)$$

since

$$\frac{(a_1 + a_2 + \ldots + a_n)}{n} = m \quad (2)$$

and therefore

$$(a_1 + a_2 \ldots a_n) = nm.$$

Substituting the value of nm in (1), we get

$$(d_1 + d_2 + \ldots + d_n) = 0, \quad (3)$$

whence it follows that the arithmetical mean is the best value to use.

50. Average Deviation of a Single Observation. — To express the accidental error that attaches to a single observation of a series, we shall use the average deviation of a single observation. This is defined as the mean of the differences between the observed values and the arithmetical mean, the individual signs of the differences being disregarded, *viz.:*

$$\text{Average deviation of a single observation} = a.d. = \frac{|d_1| + |d_2| + \ldots |d_n|}{n}.$$

This precision measure is particularly suitable for the ordinary requirements of quantitative analysis because one of the chief points in which we are interested is the concordance of the checks that obtain for a given method of analysis. Adopting then the average deviation of a single observation as our measure of precision, we will find it convenient to express this deviation as the fractional part of the arithmetical mean, stating the result in so many parts per thousand. Thus, suppose that in the standardization of hydrochloric acid by means of titration against sodium carbonate, the following values were obtained:

$$1 \text{ ml. HCl} = 0.005304 \text{ g. Na}_2\text{CO}_3$$
$$\text{``}\quad\text{``}\quad = 0.005308 \text{ ``}\quad\text{``}$$
$$\text{``}\quad\text{``}\quad = 0.005310 \text{ ``}\quad\text{``}$$

The arithmetical mean is 0.005307 g.; the individual deviations from the arithmetical mean are (without regard to sign):

$$0.000003 \text{ g.}$$
$$0.000001 \text{ ``}$$
$$0.000003 \text{ ``}$$

whence the average deviation is 0.000002 g. Expressing the average deviation as a ratio to the arithmetical mean we get 0.000002 parts per 0.005307 or 2 parts per 5,307 or 0.4 part per 1,000. This is equivalent to solving for X in the proportion

$$\frac{0.000002}{0.005307} = \frac{X}{1000}, \quad X = 0.4$$

where X is the average deviation in parts per thousand. It is more convenient to express the average deviation in parts per thousand than it is to express it in per cent because the results

of a quantitative analysis are almost always expressed in per cent, and to express the average deviation also in per cent would give rise to ambiguity. In general, the smallest limit to which we can practically reduce our error in quantitative analysis is about one part in a thousand.

51. Average Deviation of the Arithmetical Mean. — Granting that the arithmetical mean is the best representative value of a series of equally trustworthy observations when the accidental errors follow the Law of Chance, the next question that naturally arises is this: What is the magnitude of the accidental error that attaches to the value given by the arithmetical mean?

In order to answer this question we make use of the theorem proved in the Method of Least Squares that an arithmetical mean computed from n equally reliable observations is $\sqrt{n}$ times as reliable as any single observation. It follows that the arithmetical mean of 9 observations is 3 times as reliable as a single observation, and the arithmetical mean of 16 observations is 4 times as reliable as a single observation. If we represent the accidental error that attaches to a single observation of the series by u, then the accidental error of the arithmetical mean is $\dfrac{u}{\sqrt{n}}$; that is to say, the uncertainty of the arithmetical mean is inversely proportional to the square root of the number of observations. One observation has 3 times the uncertainty of the mean of 9 observations, and the mean of 4 observations has twice the uncertainty of the mean of 16 observations.

The average deviation of the arithmetical mean serves as a convenient measure of the uncertainty of the mean and can be calculated from the following relationship,

$$R = \frac{a.d.}{\sqrt{n}}$$

where R is the average deviation of the arithmetical mean, $a.d.$ is the average deviation of a single observation and n is the number of observations. A large value of the $a.d.$ for a small number of observations makes a large difference between the mean and the true value likely and consequently makes for a high degree of uncertainty of the mean. In the above illustration $a.d.$ for the

three observations was found to be 0.4 parts per 1,000. The uncertainty of the mean 0.005307 can then be calculated as follows:

$$R = \frac{0.4}{\sqrt{3}} = 0.2 \text{ parts per 1,000.}$$

52. Other Precision Measures. — Two other measures of accidental error are sometimes employed instead of the average deviation of a single observation. One of these is *The Mean Error of a Single Observation.* This is defined as the error whose square is the mean of the squares of the differences between the observed value and the arithmetical mean, *viz.*:

Mean error of a
    single observation $= \sqrt{\dfrac{d_1^2 + d_2^2 + \ldots + d_n^2}{n}}.$

The other is *The Probable Error of a Single Observation.* By the term *probable error* is meant, not the error most likely to occur, but a quantity of such magnitude that, in a given series of observations, it will be equally probable that there will be the same number of errors less than it, as there are those greater than it, the errors being arranged in order of their magnitude without regard to sign. It can be shown that the magnitude of the probable error of a single observation is given by the formula:

Probable error of a
    single observation $= 0.6745 \sqrt{\dfrac{d_1^2 + d_2^2 + \ldots + d_n^2}{n - 1}}.$

For the limiting case of an infinite number of observations, the following relationship exists among the several measures of unreliability:

Average deviation = 0.80 mean error = 1.18 probable error.

The measure of uncertainty of the mean corresponding to the mean error of a single observation is given by:

Mean error of the
    arithmetical mean $= \dfrac{\text{Mean error of a single observation}}{\sqrt{n}}.$

and that corresponding to the probable error of a single observation is given by:

Probable error of the
    arithmetical mean $= \dfrac{\text{Probable error of a single observation}}{\sqrt{n}}.$

In treating of the arithmetical mean, some writers prefer one measure, and some another; in chemistry the one that has been used most frequently perhaps is the Probable Error of the arithmetical mean, at least for atomic weight determinations.

53. Systematic Errors. — Systematic errors are errors of such a nature that they persist in a definite way from one determination to another; consequently the values of systematic errors can be more or less closely determined and their effects on the result thereby largely reduced. Sometimes systematic errors are constant in that they have the same value in successive measurements. Such an error would be produced if an object were repeatedly weighed with weights which were 5 mg. heavier than they were thought to be. Such an error is known as a *constant error*. Sometimes systematic errors are variable. Often the method of variation is definite and can be determined, whereupon a suitable correction can be applied.

Systematic errors arising from three important sources are as follows:

1. *Instrumental Errors,* due to poor construction or faulty graduation of an instrument, as, for example, the inequality in the length of the arms of a balance, the discrepancies between the indicated and the actual values of a set of weights, the inaccuracy in the graduation of volumetric apparatus.

2. *Personal Errors,* due to certain peculiarities of constitution or susceptibility on the part of individual observers, as, for instance, the habitual recording of end points too late, because of the inability to judge color changes sharply.

3. *Errors of Method,* due to causes such as incorrect sampling; incompleteness of precipitation; contamination of precipitates by impurities; the incompleteness of oxidation-reduction reactions, resulting in an appreciable difference between the equilibrium point of a reaction and the equivalence point as represented by the stoichiometric equation; the excess of standard solution necessary to establish the end point in a volumetric determination, etc.

Even when the utmost care is exercised it is not possible to determine the true value of a measured quantity, but only a more or less close approximation to it. Consequently, we cannot determine the difference between the measured value and the

true value. It is not easy, therefore, to define what shall constitute the measure of a systematic error. It is obvious that, since the true value itself cannot be ascertained, it becomes necessary to select the closest approximation to the true value that is possible. This is done by taking the average of the observed values obtained in any given case by the best workers, with the most refined instruments and methods and with all the effects of error reduced as far as possible.

In the case of determinations in which a pure salt can be used as the starting point, this "closest approximation to the true value" can be arrived at by the employment of the proper stoichiometric equations and the most recent values for the atomic weights.[3] The value thus obtained is known as the "theoretical value."

In the case of certain determinations where the use of pure salts would not parallel the actual conditions, the Standard Analyzed Samples of the Bureau of Standards[4] furnish the "closest approximation to the true value" that we have.

The difference between the average value (arithmetical mean) that a worker is able to obtain and the "closest approximation to the true value" shows the magnitude of the systematic errors in his determination. We shall therefore adopt as the measure

[3] It is well to bear in mind that even the atomic weights themselves have not been rigidly fixed. Thus a comparison of the atomic weight table for 1914 (*J. Am. Chem. Soc.*, **36**, 1587) and that for 1921–22 (*ibid.*, **43**, 1752) shows that of fifteen of the elements commonly met with in quantitative work (Al, Ca, C, Cl, Cu, I, Fe, Pb, Mn, N, P, K, Ag, Na, S), three (C, Pb, S) have had their atomic weights changed during this seven-year period to the extent of about one-half part per thousand, while one (Al) has been changed four parts per thousand. For similar changes from 1907 to 1912 see *Nat. Bur. Standards*, *Circular* No. 40, "Sodium Oxalate as a Standard in Volumetric Analysis," p. 11 (1913).

[4] See *Nat. Bur. Standards*, *Circular* No. 25, "Standard Samples," General Information, June 29, 1922, Washington, D. C. Also *Supplement to Circular* No. 25, Oct. 6, 1924. The Bureau has prepared the following samples which they supply in small quantities at a nominal charge with the understanding that samples be used only as ultimate standards. Their list comprises Irons, Steels, Alloy Steels, Ferro Alloys, Sheet Brass, Bronzes, Bearing Metals, Argillaceous Limestone, Zinc Ore, Manganese Ore, Lake Superior Iron Ores, Magnetite Iron Ore, Tennessee Phosphate Rock; also Sugars, Naphthalene, Benzoic Acid and Sodium Oxalate.

of the magnitude of the systematic error, the ratio of this difference to the "closest approximation to the true value," and shall express this ratio in so many parts per thousand.

As an illustration to show how we compute the accidental error as well as the systematic error which attaches to a determination, let us take the results of M. van't Kruys, *Z. anal. Chem.* **49,** 413 (1910), in his study of the influence of certain salts upon the quantitative determination of sulfates as barium sulfate. This worker obtained the following weights of barium sulfate from 25.00 ml. 0.05 M K$_2$SO$_4$ + 25.00 ml. 0.05 M BaCl$_2$: 0.2890, 0.2885, and 0.2883 g.

The average is 0.2886 g.; the average deviation is 0.0003 g. or 1 part per 1,000 which gives us the accidental error. The theoretical value is 0.2919 g., which is obtained by solving the following proportion for x,

$$K_2SO_4 : BaSO_4 :: 0.2179 : x$$
or
$$174.27 : 233.44 :: 0.2179 : x.$$

The systematic error is then the difference between 0.2886 g. and 0.2919 g., or 33 parts per 2,919 or 11 parts per 1,000, the results being low. This example is a very good illustration of the fact that concordance of checks is not necessarily a proof of freedom from error. The checks may agree excellently and there still be a large constant error.

54. The Significance of the Average Deviation. — If all the errors in a measurement were accidental errors, then by making a sufficient number of these measurements, so that the deviations followed the probability curve, we could establish, by means of
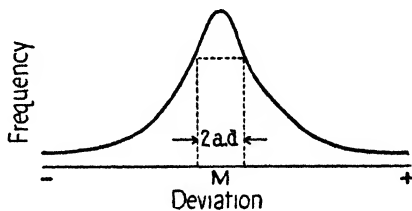
Fig. 18

Probability Curve

When all errors are accidental the true value lies within 2 *a.d.*

the average deviation of a single observation, the limits within which the true value would lie. This is illustrated in Figure 18 where M is the mean of the measurements and *a.d.* is the

average deviation of a single observation. 2 *a.d.* represents the limits within which the true value lies. By way of illustration, if a sufficiently large number of weighings of a piece of metal yields a mean value of 0.4002 g. and an average deviation of 0.0001 g., then, if all the errors involved are accidental we can conclude that the true weight of the piece of metal is very close to the mean of the measurements and is between 0.4001 g. and 0.4003 g.

If all the errors in the series of measurements were accidental errors, then from the average deviation of a single observation, *a.d.*, and the number of measurements, *n*, we could obtain the measure of the uncertainty of the mean of our results for:

$$R = \frac{a.d.}{\sqrt{n}},$$

where the average deviation of the arithmetical mean, *R*, is our measure of uncertainty.

On the other hand, the measurements might involve not only accidental errors but also some constant error for which no correction has been applied. The average deviation of a single observation calculated from these measurements does not necessarily establish limits between which the true value lies.
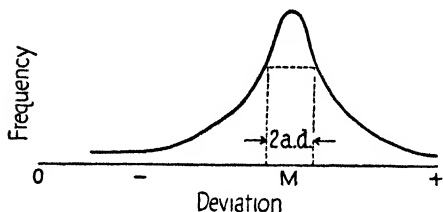
Fig. 19

Probability Curve

When systematic errors are involved the true value
may not lie within 2 *a d.*

If, in the previous illustration, one of the weights used in making each of the weighings was actually 0.0010 g. lighter than was supposed, then the curve of the above figure would be displaced to the right an amount corresponding to a constant error of 0.0010 g.   This is illustrated in Figure 19 where *0* is the point of zero error or the true value, *M* is the mean of the measurements and *a. d.* is the average deviation of a single observation. Obviously, the true value does not lie within the limits measured by 2 *a.d.* If we incorrectly assume that no con-

stant error is present and if $M = 0.4012$ g. and $a.d. = 0.0001$ g., we must conclude that the true value lies between 0.4011 g. and 0.4013 g. The constant error involved is about 2.5 parts per 1,000 while the accidental error is only 0.25 parts per 1,000. Under these circumstances, a small average deviation is no assurance that the mean is very close to the true value. It merely serves as a measure of the accidental error and the reproducibility of our results. Likewise, the uncertainty of the mean of our results as measured by R cannot be determined when a constant error is involved.

It should be evident that the chemist must be always on the lookout for systematic errors, which, when detected, should be corrected for. After all the corrections have been made for the systematic errors which are known to be present, it should be borne in mind that one or more systematic errors may have escaped detection and that a small average deviation is not conclusive evidence that the mean is very close to the true value. Under these circumstances, we are forced to use the mean as the best representation of the true value or to resort to some other method of determination.

55. Effect of Errors in Primary Measurements upon Derived Result. — It has already been pointed out that the ultimate error with which we are concerned in any given determination is a function of the errors which exist in the primary measurements. For a final result to be free from error, it would be necessary that all the primary measurements themselves be free from error. Evidently this is an impossibility. Hence, granting a certain allowable limit of error in the final result, it can be seen that the real point of concern is this; namely, that the errors in the primary measurements shall be compatible with the precision desired in the final result.

Now the way in which primary errors enter into the final result depends upon the functional relationship which exists between the final result and the primary measurements. These relationships are treated of in detail in more advanced treatises on precision, but, for our purpose, such a treatment is not necessary since it will serve our ends equally well to make use of the generalization which is there established, namely, that in order to

obtain the desired degree of precision in a determination, when the operations are those of *multiplication* and *division*, the primary measurements shall each contain no less a number of significant figures than is desired in the final result. The precision of the final result cannot be greater than the precision of the least precise factor. When the operations are those of *addition* and *subtraction*, the last digit which we wish to retain in the final result must correspond to the first doubtful digit in any of the primary measurements. In the case of addition, the final result will have a precision between that of the most precise and least precise terms, as shown in the following example:

Terms	*Precision*
100.0 mg. $\pm$ 0.1 mg.	1 part per 1,000
10.0 mg. $\pm$ 0.1 mg.	10 parts per 1,000
110.0 mg. $\pm$ 0.2 mg.	1.8 parts per 1,000

Thus, the actual value of the precision of the final result will depend on the magnitude and precision of each of the terms.

In the case of subtraction, the precision of the final result will never be better than that of the most precise term and it may be worse than that of the least precise term. This is illustrated by the following example:

Terms	*Precision*
40.00 ml. $\pm$ 0.02 ml.	0.50 parts per 1,000
30.00 ml. $\pm$ 0.02 ml.	0.67 parts per 1,000
10.00 ml. $\pm$ 0.04 ml.	4.00 parts per 1,000

The problem of seeking beforehand to arrange our experimental details so that the primary measurements will have a sufficient number of significant figures to give the desired precision in the final result is often referred to as the *Converse Problem*. It should always be given careful consideration with respect to every analytical procedure or determination.

As an illustrative example showing the application of the Converse Problem, let it be required to fix the quantity of sodium carbonate which should be weighed out for the standardization of approximately 0.1 M hydrochloric acid by means of titration,

knowing that in the final result we are aiming at a precision of
1 part per 1,000, that we can weigh the sodium carbonate precisely
to 0.1 mg. and can measure the volume of the hydrochloric acid
to within 0.02 ml.   Let us assume also that methyl orange is the
indicator, that the titration is carried out in triplicate and that
the errors involved are accidental errors.   Letting E equal the
error in the final result, e_1, e_2, etc., the component errors contrib-
uting toward the error in the final result, and m the number of
component measurements, we have

$$E = \sqrt{e_1^2 + e_2^2 + \ldots e_m^2}.$$

When n repetitions of the experiment are performed, the error
in the final result of each must be $E\sqrt{n}$, if the error in the mean
of n repetitions is to be E.   We have then

$$E\sqrt{n} = \sqrt{e_1^2 + e_2^2 + \ldots e_m^2}.$$

Assuming that the component errors produce equal effects on
the error in the final result, we have

$$e = \frac{E\sqrt{n}}{\sqrt{m}}.$$

For the case in hand, the component measurements are the
measurement of the weight of Na_2CO_3 and the measurement of
the volume of HCl solution.   If the error, E, in the final result
of the standardization of the HCl solution is not to exceed 1
part per 1,000, we have for triplicate titrations

$$e = \frac{1 \times \sqrt{3}}{\sqrt{2}} = 1.21 \text{ parts per 1,000.}$$

Since an error of 0.0001 g. is involved in the weighing, then
the weight of Na_2CO_3 required, as far as the weighing operation
alone is concerned, is obtained from

$$\frac{1.21}{1,000} = \frac{0.0001}{X}$$

whence

$$X = 0.0826 \text{ g. of } Na_2CO_3.$$

Since an error of 0.02 ml. is involved in the burette reading, then the volume of HCl solution required, as far as the volume measurement is concerned, is obtained from

$$\frac{1.21}{1,000} = \frac{0.02}{X} \quad .$$

whence

$$X = 16.4 \text{ ml. of HCl solution.}$$

Now it is known that when methyl orange is used as the indicator 2 HCl is required to titrate each Na_2CO_3 present, consequently 2,000 ml. of molar hydrochloric acid, which contains 2 HCl, is required for 106.0 g. of Na_2CO_3. It follows that 20.00 ml. of $0.1000 M$ HCl is required for 0.1060 g. of Na_2CO_3. The weight of Na_2CO_3 required for 16.4 ml. of $0.1000 M$ HCl solution is obtained from

$$\frac{20.00}{0.1060} = \frac{16.4}{X}$$

whence

$$X = 0.0869 \text{ g. of } Na_2CO_3.$$

When the number of component measurements, m, is small, as it is in the above example, there is considerable risk in applying the Law of Chance. It is therefore desirable to weigh out more than the calculated amount of substance. In the foregoing standardization it is advisable to use about twice the calculated weight of Na_2CO_3, or about 0.174 g.

56. Minimization of Errors. — Accidental errors from their very nature have to stand as encountered, but systematic errors often can be very materially reduced, this minimization being accomplished either directly, by means of calibration, or by running a blank, or, indirectly, by running a control.

Calibration. — This applies to instruments and consists in comparing the instrument with a known standard and determining the errors of the scale divisions or units as accurately as possible, and then, instead of trying to adjust the instrument, applying the appropriate correction to the original measurement. In this connection it cannot be emphasized too strongly that every chemist should calibrate his set of weights and his volumetric apparatus, because of the inaccuracies that are invariably present.

Running a Blank. — This consists in running a separate determination to find out the effect of the impurities in the reagents, or to find the excess of standard solution necessary to establish the end point under the conditions met with in the titration of the unknown sample.

Running a Control. — This consists in making a determination under as nearly like conditions as possible in regard to volume of solution, concentration of reagents, temperature, routine of procedure, and any other determining factor, upon a known quantity of standard substance containing sensibly the same weight of constituent being determined as that contained in the sample of the unknown taken for analysis.

The weight of constituent in the unknown is then calculated from the proportion:

$$\frac{\text{Result found for standard}}{\text{Result found for unknown}} = \frac{\text{Weight of constituent in standard}}{X}$$

where X stands for the weight of constituent in the unknown.

In order to show to what extent the constant error is reduced by this procedure, let r be the constant error of the method. Let V be the theoretical chemical equivalent corresponding to the weight of constituent in the standard solution, and let V' be the theoretical chemical equivalent of the weight of the unknown substance. The values in Table 7, arrived at by means of calculations presented in the Appendix, gives us a means of finding the error resulting from various ratios of $\frac{V}{V'}$ and $\frac{r}{V}$.

Table 7

CONSTANT ERRORS FOR VARIOUS RATIOS OF EQUIVALENTS OF CONSTITUENT
IN STANDARD SOLUTION AND UNKNOWN SUBSTANCE

Ratio $V : V'$	Ratio of $r : V$				
	1/1000	1/500	1/100	1/50	1/20
	Error in parts per 1,000				
0.4	3/5	1⅕	6	12	30
0.6	2/5	4/5	4	8	20
0.8	1/5	2/5	2	4	10
1.0	none	none	none	none	none
1.2	1/5	2/5	2	4	10
1.4	2/5	4/5	4	8	20
1.6	3/5	1⅕	6	12	30

It will be noticed from the foregoing table that the error is greater, the greater the ratio $\dfrac{r}{V'}$ or the more the ratio $\dfrac{V}{V'}$ differs from unity. This fact is brought out very clearly if we use the graphical mode of representation, as shown in Figure 20.
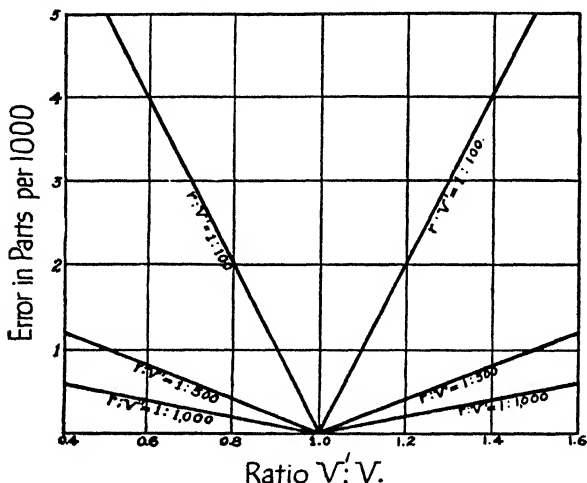
Fig. 20

Constant Errors for Various Ratios of Equivalents of Constituent in Standard Solution and Unknown Substance

An important application of this principle is in volumetric analysis. Here the value of a standard solution is first found by titrating a certain number of milliliters of it, $V + r$, against a known weight W of some suitable standard substance. In this case V represents the number of milliliters corresponding to the theoretical point of the reaction while r represents the number of milliliters excess or defect of reagent with respect to the theoretical point when the end point has been established.

The value so found, $\dfrac{W}{V + r}$, is then used as a factor to multiply the number of milliliters, $V' + r$, of the standard solution used in titrating the unknown, the result being assumed to be the weight X of the constituent sought, namely,

$$\frac{W}{V + r}(V' + r) = X.$$

[76]

It follows from what has already been said that X will be independent of the error r that occurs in $(V + r)$ and $(V' + r)$ if the same number of milliliters of standard solution has been used in the unknown titration as in the standardization; it will, however, still be affected by the error in W. If, as is generally the case, a different number of milliliters of standard solution has been used in the unknown determination and the standardization, then X will be affected by both the error r and the error in W.

57. Number of Observations. — We have seen that the accidental error of the arithmetical mean of a series of observations is inversely proportional to the square root of the number of observations. From this fact, and the further fact that the accidental error of the arithmetical mean is usually small with respect to the arithmetical mean, it follows that a point will soon be reached when the decrease in the magnitude of the error does not compensate for the time and labor necessary to make the further observations. Thus, if R represents the accidental error of the arithmetical mean corresponding to n determinations, then the uncertainty of the mean and the error corresponding to $2\,n$ determinations, $3\,n$ determinations, etc., will be:

No. of determinations	n	$2\,n$	$3\,n$	$4\,n$	$5\,n$
Accidental error of arithmetical mean	R	$0.71\,R$	$0.58\,R$	$0.50\,R$	$0.45\,R$

For atomic weight work, the number of determinations is usually eight to ten; for establishing the precision of a method, the number is four to six for each variable factor that has to be considered in relation to the method; for standardizing solutions, the number is three to four; and for analyses in general, the number is one to three, depending upon the precision of the method that is used and upon the precision that is required for the purpose in hand.

58. Rejection of an Observation. — It sometimes happens in a series of observations that one of the determinations will differ very widely from the rest without any apparent mistake having been made in the work. It then becomes a question as to whether or not to include this result with the others in obtaining the value of the arithmetical mean. A good criterion, in such a case, which

is applicable only when at least four determinations including the doubtful one have been made, is the following: Omit the doubtful observation and compute the arithmetical mean and the average deviation of the other observations.   Then compute the difference between the doubtful observation and the arithmetical mean of the observations which are not doubtful.   If this difference is four or more times the average deviation of the other observations, reject the observation, since it can be shown from the theory of probability that the chances are 993 in 1,000 that such an observation is the result of a mistake.[5]

By way of illustration, suppose that in standardizing hydrochloric acid by means of sodium carbonate, the following data were obtained:

| | Grams of Na_2CO_3 Equivalent |
Sample	to One ml. of HCl
1	0.005316
2	0.005311
3	0.005303
4	0.005315

Tentatively rejecting Sample 3 as being doubtful, we obtain the average deviation of the remaining results as follows:

Sample	Grams of Na_2CO_3 Equivalent to One ml. HCl	Deviation
1	0.005316	0.000002
2	0.005311	0.000003
4	0.005315	0.000001
	Mean 0.005314	a.d. 0.000002
	0.005303	

$$0.000011 > 4 \times 0.000002 = 0.000008$$

Therefore, Sample 3 will be permanently rejected.

[5] J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," 4th ed., p. 533, Longmans, Green & Co., New York, 1931.

59. Examples.

1. The Committee on Uniformity in Technical Analysis, *J. Am. Chem. Soc.*, **26**, 1648 (1904), show in their report that a sample of oxidized ore from New Jersey, containing franklinite, willemite and zinc spinels, and having a zinc content of 18.16%, was analyzed by forty-two chemists with results varying from 12.20 to 39.22%. Twenty-three of the chemists were or had been in zinc works, three in other works where zinc was frequently determined, eleven were commercial chemists most of whom made a specialty of zinc, and five were professors or instructors in colleges. There were eight methods used.

Analyst 33 found 12.20, 12.73 and 13.74% Zn. What was his average deviation and what his constant error?

> Ans. Average deviation 44 parts per 1,000.
> Constant error 290 " " " (results low).

Since each analyst must have been satisfied with the concordance of his own results, it is evident from the above report that the concordance of a series of determinations made under similar conditions is in itself no criterion of the absence of a constant error, and often this constant error may be very large in amount.

2. In standardizing $AgNO_3$ solution by means of pure sodium chloride, the following data were obtained. Determine whether any of the results should be rejected and calculate the average deviation in parts per 1,000.

No. of Experiment	Grams NaCl Equivalent to One ml. of $AgNO_3$ Solution
1	0.005824
2	0.005825
3	0.005826
4	0.005823

3. In determining the amount of phosphorus in a sample of disodium phosphate, having the formula $Na_2HPO_4 \cdot 2H_2O$, the following percentages, calculated as PO_4, were obtained: 52.58, 52.86, 52.52, 52.83, 52.47, 52.71, 52.43, 52.79, 52.32, 52.64, 52.39. What is the average deviation and what is the constant error? Should any of the determinations be rejected?

> Ans. Average deviation 3.1 parts per 1,000.
> Constant error 15.1 " " " (results being low).
> None of the results should be rejected.

4. Richards and Hoover in their article, "The Molecular Weight of Sodium Sulphate and the Atomic Weight of Sulphur," *J. Am. Chem. Soc.*, **37**, 112 (1915), give the following figures for the ratio between sodium carbonate and sodium sulfate:

No. of Experiment	Weight of Na_2SO_4 from 1.00000 g. Na_2CO_3
1	1.34014 g.
2	1.34016 g.
3	1.34013 g.
4	1.34019 g.
5	1.34015 g.
6	1.34018 g.

What is the average deviation?   Should any of the results be rejected?

Ans.   Average deviation 0.013 parts per 1,000.
None of the results should be rejected.

5. In standardizing an approx. 0.1 M silver nitrate solution for use in Mohr's method for determining chloride, the following results were obtained by a student:

Gram NaCl Used	ml. Silver Nitrate Solution Required
0.2090	34.20
0.2102	34.48
0.2381	39.03
0.1969	32.37

What was the average deviation?   Should any of the observations be rejected?   Ans.   Average deviation 1.2 parts per 1,000.
No observation should be rejected.

6. In the Eschka method for sulfur in coal, 1 g. of coal, 1 g. of MgO and 0.5 g. of Na_2CO_3 were used.   The weight of $BaSO_4$ obtained was 0.3236 g. A blank analysis on a mixture of 10 g. of the MgO and 5 g. of the Na_2CO_3 yielded 0.0921 g. of $BaSO_4$.   What was the percentage of sulfur in the coal?   Ans.   4.30%.

7. Yagoda and Fales, in their article, "The Separation and Determination of Tungsten and Molybdenum," *J. Am. Chem. Soc.*, **58**, 1494 (1936), report the following:

Separation of MoS_3 from Tungsten

Experiment	$Na_2MoO_4 \cdot 2H_2O$	$Na_2WO_4 \cdot 2H_2O$	White Molybdic Oxide Recovered
1	0.0513	. . . . .	0.0304
2	0.0516	0.0516	0.0300
3	0.0509	0.5013	0.0298
4	0.0524	0.5031	0.0303
5	0.1698	. . . . .	0.1013
6	0.17	0.2026	0.1014

Calculate the theoretical amounts of molybdic oxide for the several experiments, and the differences in parts per 1,000 between the calculated and actual results.

CHAPTER IV

WEIGHING [1]

60. General Considerations. — Most quantitative processes resolve themselves, in effect, into two determinations of mass, that of the sample being analyzed and that of the constituent being sought, because it is the ratio of these masses which is the object of nearly every quantitative analysis. By mass is meant the quantity of matter which a body possesses.

Now the determination of mass rests upon the fundamental principle that an object of which mass is M is attracted by the earth with a force F which is proportional to the product of the mass and the intensity of gravity g which is acting upon the mass, namely,

$$F = Mg. \tag{1}$$

If we have two bodies of respective masses M_1 and M_2, then the corresponding gravitational forces F_1 and F_2 would be

$$F_1 = M_1 g \tag{2}$$
$$F_2 = M_2 g. \tag{3}$$

From this it follows that if the intensity of gravity is the same in both cases, as it always is, when the two bodies are in the immediate locality of each other, the following relationship is true:

$$\frac{F_1}{F_2} = \frac{M_1}{M_2}, \tag{4}$$

or, in other words, the ratio of the respective gravitational forces is equal to the ratio of the corresponding masses. For the special case where this ratio is unity, we have as a consequence that

$$F_1 = F_2 \text{ and } M_1 = M_2, \tag{5}$$

or, in other words, when the gravitational forces are equal the masses are equal.

[1] For a great deal of very valuable detail, which it is felt is beyond the scope of this book, the reader is referred to the *Nat. Bur. Standards, Circular* No. 3, "Design and Test of Standards of Mass," 3rd ed., Washington, 1918.

Strictly speaking, the force of gravity acting on a body is its weight. Since this force varies with the intensity of gravity g, and since g varies with the locality, it follows that the weight of a body is dependent on its locality. The mass of a body, however, being the quantity of matter it possesses, is independent of the locality. Unfortunately, common usage has extended the meaning of the term *weight* to include mass as well. This usage, confusing and misleading as it is, seems to be too firmly established to correct, consequently the term *weight* will often be used in the succeeding discussions to mean *mass*. When weight, in the strict sense, is intended, it will be described as the force of gravity acting on a body.

61. Standard of Mass. — The fundamental standard of mass which has been adopted by the principal governments of the world is the *International Prototype Kilogram,* which is a mass of platinum-iridium made in 1887 and deposited in the International Bureau of Weights and Measures near Paris. The kilogram represents as exactly as possible the mass of one liter of water at 4°C. Two authentic copies of this standard are kept in a vault at the National Bureau of Standards, Washington. They are known as *National Prototype Standards of Mass,* and are used only when needed to verify the secondary standards of the Bureau.

The Unit of Mass that is almost invariably employed in laboratory work, however, is not the kilogram but the gram, which is the one thousandth part of the kilogram. This unit is consequently equal to the mass of one cubic centimeter of water at 4°C.

62. Reference Masses. Weights. — Weights often come in graduated sets, of which the largest weight is 100 or 50 g. and the smallest 1 mg. It is seldom, however, that the 100 g. weight will be required. The usual denominations that are employed for a set of weights are as follows:

Grams   100,   50,   20,   10, 10,   5,   2,   2, 1
Milligrams 500, 200, 100, 100, 50, 20, 10, 10, 5, 2, 2, 1.

In addition to the weights, a set should include one or two "riders," which are small weights made of platinum wire for use on the beam of the balance. The larger weights, down to and including the 1 g. weight, are generally constructed of brass

and plated with gold, platinum, nickel or chromium, or coated with lacquer to prevent corrosion; the smaller or fractional weights are of platinum, aluminum, tantalum or German silver. It cannot be too strongly stressed that no set of weights, no matter how fine they look nor how much they cost, should be considered as correct until they have been carefully calibrated, and, even after a set has been calibrated, it must be borne in mind that the values change more or less with time so that a recalibration should be made at least once a year. The method of calibration will be described in §§ 91 to 95.

63. The Equal-arm Balance. — The equal-arm balance consists essentially of a metal beam mounted at its center upon a prism knife-edge and carrying at each end a terminal knife-edge. The central knife-edge rests upon an agate plate and the terminal knife-edges each support a suspension which carries a pan. One pan serves to carry the object and the other to carry the reference masses or weights. Figure 21 illustrates these features. The mass M_1 of a body can be determined by placing the body on the left-hand pan and balancing with reference masses on the right. If M_2 represents the sum of the reference masses used,

Fig. 21

Equal-arm Balance, Showing Essential Features

F_1 and F_2, the forces of gravity acting on M_1 and M_2, and L and R the left and right arms of the balance, then, from the principle of the lever, it follows that

$$F_1 L = F_2 R.$$

Since $L = R$, it follows that $F_1 = F_2$. We have already seen that when the gravitational forces are equal, the masses are equal. It follows therefore that

$$M_1 = M_2.$$

We have assumed throughout this discussion that gravity is the only force acting on our system.   In point of practice, however, forces due to the buoyant effect of the air are encountered. In many quantitative determinations the precision required is sufficiently low to make consideration of these forces unnecessary.
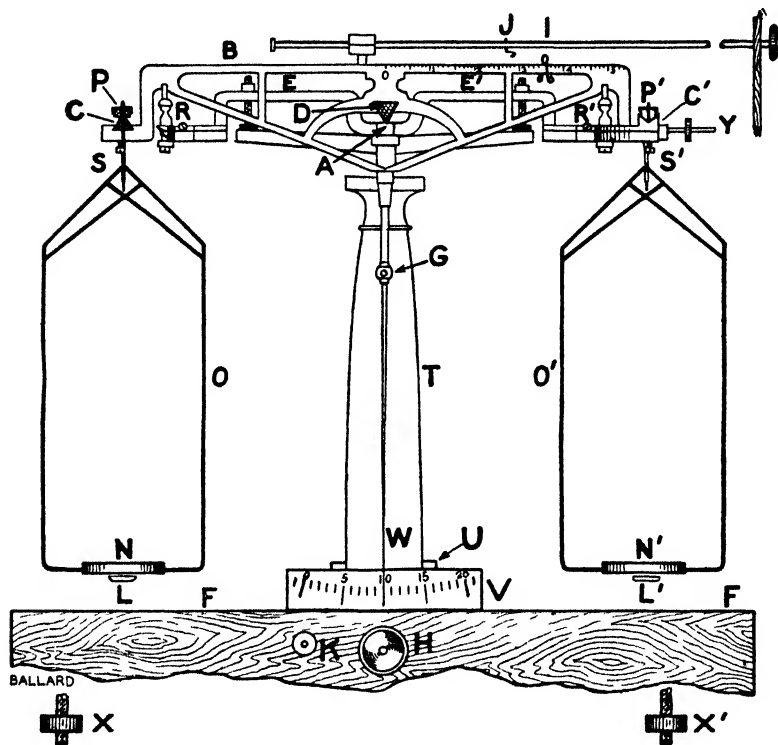
Fig. 22

The Equal-arm Beam Balance, Showing Details of Construction

Where a high degree of precision is required, these forces must not be disregarded.   They will be considered in § 79.

The details of an equal-arm balance are shown in Figure 22. The column T, which is anchored to the floor F, carries the agate plane A.   The beam B is mounted at its center upon the central prism-edge D; at the ends of the beam B are the terminal prism-

edges C and C' which carry the small agate planes P and P'. These latter serve to mount specially constructed stirrups S and S' which carry the balance pans N and N' through the bow strings O and O'. In order to protect the bearing edges of the prisms D, C and C' from wear, balances are provided with two sets of rests known respectively as "beam rests" and "pan rests." The beam rests R and R' are attached to the movable arms E and E' which are hinged to the column T and are operated by means of the milled head H placed at the center of the balance just below the floor F of the balance. When the head H is rotated, it turns a cam which raises a rod passing through the column T; this rod in turn raises the arms E and E' until the studs R and R' engage corresponding studs in the beam B and cause enough of a movement to bring the central prism-edge clear of the agate plane A; at the same time the stirrups S and S' are engaged by the ends of the arms E and E' and lifted clear of the terminal prisms C and C'. This whole arrangement is so disposed that each time the beam is raised and lowered the several parts are brought back into exactly the same alignment.

The pan rests L and L' are controlled by means of a small push-button K placed to one side of H. When the button is pushed in, the rod to which it is attached moves a lever (not shown in diagram) which causes the arms carrying L and L' to drop so that the pans are free to move up and down. At all times when the balance is not swinging the pan rests should be in their raised position so as to keep the pans from moving about and so protect the terminal prisms C and C' from needless wear. If when the pan arrests, L and L', are raised they do not touch the pans, they may be adjusted by means of thumb screws on L and L'.

While we shall give a set of rules in § 64 for the use of the balance, we would drive home the idea at this juncture that in operating a balance it should always be handled so that edges of the prisms are brought down gently and lifted gently from their bearings. If this care is not exercised and the prism-edges are brought down roughly, it will take only a month or so before the balance will be unfit for use.

Besides the parts already discussed there should be mentioned the pointer W which is attached to the beam and which plays

over the graduated scale V.   If the scale is not already numbered, it should be numbered,[2] as illustrated in Figure 22.

The weight G is a small weight which can be moved up or down on the pointer W when it is desired to increase or decrease the sensibility of the balance.   The rider rod I and the rider hook J are used to manipulate the "rider," which is a small piece of platinum wire bent in such form as to hang on the beam of the balance and be easily movable from one position to another on the beam.   The rider is used in the final adjustment of weights in a weighing when the necessary adjustment lies within 5 mg., thus obviating the troublesome manipulation of the very small 1 and 2 mg. weights.   The leveling screws X and X' are used to level the balance as indicated by the leveling plate U.   The adjusting screw Y on the beam is used for the purpose of adjusting the equilibrium position of the balance so that the needle shall rest sensibly at the middle point of the scale V.

64. Directions for the Use of the Balance. --

1. The balance should be set up on a solid platform fixed to a wall or to a pier which is as free from mechanical vibration as possible; to further reduce vibration it is advisable to interpose glass cups mounted on rubber stoppers between the legs of the balance and the platform.   A place should be chosen where neither direct sunlight, nor hot nor cold draughts, will come in contact with the balance, as resulting temperature changes will produce errors in the weighings.

2. When not in use, the beam arrests and the pan supports must be up so that the prism-edges are free of contact with their opposing planes, otherwise injury to the edges will result from jarring.

3. In releasing the balance, first bring the prism-edges into contact with their opposing planes very carefully and gently; then lower the pan supports and start the balance swinging by wafting down a gentle current of air on the right-hand pan by a few quick impulses of the hand.   Never touch the pan with the

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[2] In accordance with the recommendation of Kohlrausch, "Leitfaden der praktischen Physik," 44, Leipzig, 1896.   It is also an advantage to have a scale with red lines, as pointed out by C. M. Clark, *J. Am. Chem. Soc.*, **32**, 884 (1910).

forceps nor attempt to start the beam swinging by suddenly lowering it upon its prism-edges.

4. As the first step of a weighing, always ascertain the zero point of the balance. If it is more than one division away from the center point of the scale, proper adjustment should be made by turning the small nut Y on the right-hand beam. *The student, however, should not make this adjustment himself, nor any other adjustment that might be needed, but should bring the matter to the immediate attention of the instructor.*

5. Upon any occasion when objects are being added to or removed from the pans, both the beam arrests and pan supports must be raised so as to protect the prism-edges.

6. As the last step in a weighing, first bring the pans to rest by raising the pan supports just when the needle passes by the center of the scale. Then raise the beam very carefully and gently, remove the weights and the object, and finally close the balance case.

7. No chemicals, minerals, salts or like substances which can possibly injure the balance pans should ever be placed directly upon them, but upon a watch-glass or in some suitable vessel like a weighing bottle or crucible. The practice of keeping an open dish of concentrated sulfuric acid or anhydrous calcium chloride to maintain a dry atmosphere inside the balance case has been shown by O. Kuhn[3] to be of no value and should be avoided as it endangers the balance through the possibility of the dehydrating agent overflowing or upsetting.

8. Objects should never be weighed while hot, as the air currents produced inside the balance case will introduce very serious errors in the weighing.

9. The weights should be handled *only* with the pincers provided for that purpose. The large weights should be placed near the center of the pan and the fractional weights should be arranged on the pan in some systematic order with respect to their denominations.

10. Care should be taken not to overload a balance by weighing bodies heavier than those which the balance is designed to carry (cf. § 66).

[3] O. Kuhn, *Chem.-Ztg.* **34**, 1097 (1910).

65. Obtaining the Zero Point with Empty Pans. — The zero point, also called rest point or point of equilibrium, is the position of rest of the pointer when both pans are empty. To determine the zero point the balance pans should first be dusted free of any dust by means of a camel's-hair brush; the beam arrest is then lowered gently by turning the milled head in front of the balance case, after which the pan arrests are lowered by pushing in the button alongside of the milled head. The balance is now free to vibrate, and, to bring this about, the balance door is lifted about five inches and a slight current of air fanned down on the right-hand pan by means of a few impulses of the hand. With a little practice it is possible to control matters so that the pointer can be brought over to any desired division on the scale; usually we aim to bring it somewhere near five or six. The door of the balance is closed and the pointer allowed to swing back and

forth several times. The zero point is then determined by taking one more reading of the left-hand extremities of the arcs through which the pointer swings than is taken of the right-hand extremities. Usually three readings are taken on the left side and two on the right. These two sets of observations are averaged separately and the mean of these averages taken. This mean value is called the zero point. An illustration shows that the calculation is very simple:

	Left			Right	
1st	reading	5.2	1st	reading	15.1
2nd	"	6.0	2nd	"	14.3
3rd	"	6.6		Average	14.7
	Average	5.9			5.9
				2)20.6	
				Zero point	10.3

The reason for taking an odd number of readings on one side

Fig. 23

Oscillations of the Equal-arm Balance

and an even number on the other is found in the fact that the balance oscillates about the prism-edge like a compound pendulum. The oscillations are damped by friction in the bearings and by air resistance; hence, each swing will be a trifle shorter in length than the preceding one, as illustrated diagrammatically in Figure 23. The final position of the pointer will, therefore, not be exactly halfway between the average of the turning points on the left and the average of the same number of points on the right, but halfway between the average of $n + 1$ points on the one side and n points on the other.

The validity of our procedure for obtaining the zero point by taking the average of an odd number of readings on one side and an even number on the other, and obtaining the mean of these two averages for our zero point is demonstrated by calculations given in the Appendix.

66. Sensibility. — The sensibility of a balance or the angle α (Figure 24) through which the balance turns for a given excess
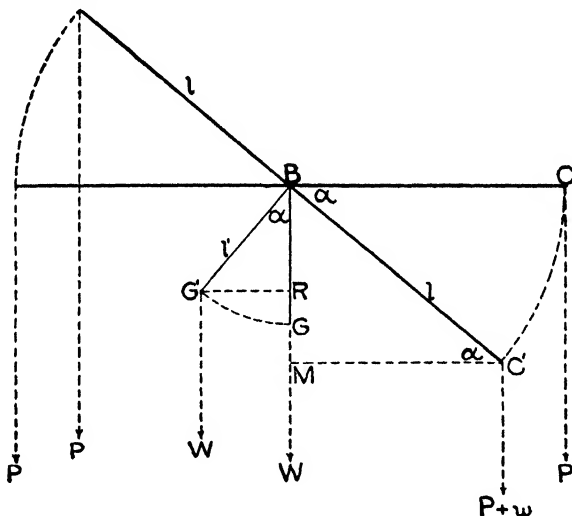
Fig. 24
Principle of Balance Arms

of weight, w, in one pan or the other depends upon the following factors (ignoring friction): on w, the given excess of weight; on l,

half the length of the beam; on W, the weight of the beam and pointer and everything rigidly connected to it; also it depends on l', the distance of the center of gravity of the balance below the central prism-edge, according to the relationship:

$$\alpha \text{ (in radians)} = \frac{wl}{Wl'}$$

Proof: Taking moments about B, assuming both arms equal,

$$(P + w)C'M = P(C'M) + W(G'R)$$

$$(P + w - P)C'M = W(G'R)$$

$$C'M = \frac{W(G'R)}{w}$$

or,

$$\frac{1}{C'M} = \frac{w}{W(G'R)}.$$

Multiplying both sides of the last equality by (BM), we get

$$\frac{BM}{C'M} = \frac{w(BM)}{W(G'R)}.$$

Now the triangles $BC'M$ and BRG' are similar, therefore

$$BM : G'R :: l : l'.$$

Making use of this proportion and remembering that $\dfrac{BM}{C'M} = \tan \alpha$,

we get

$$\tan \alpha = \frac{wl}{Wl'},$$

or since for small angles, such as we encounter in the swings of a balance, $\tan \alpha = \alpha$, we have finally

$$\alpha \text{ (in radians)} = \frac{wl}{Wl'} \qquad \text{Q. E. D.}$$

From this equation it follows that:

1. The longer the beam, the greater the sensibility.

2. The lighter the beam, the greater the sensibility.

3. The smaller the distance between the point of suspension of the balance and the center of gravity, the greater the sensibility.

Unfortunately, the preceding conditions for maximum sensitiveness conflict with one another in the mechanical construction

of a balance. Thus long arms are incompatible with minimum weight. The length of the arms is also practically limited by another condition, namely, the time of swing of the balance, which must not be excessive. If a balance is regarded as a compound pendulum, it can be shown that its time of vibration is given by the expression

$$t = 2\pi \sqrt{\frac{Wk^2 + 2Pl^2}{Wl'g}}$$

where k = radius of gyration of beam and pointer,
P = weight of pan with load,
g = acceleration due to gravity, and W, l, and l' have the same significance as before.

From this equation it will be seen that a limit is soon reached beyond which it is undesirable to increase the sensitiveness of a balance by increasing the length of its arms, l, for its time of vibration becomes excessive, and the process of weighing, very tedious. A time of swing of 12 to 15 seconds is about the maximum time desirable. Again, the sensitiveness cannot be increased by diminishing l' beyond a certain limit for the same reason. The center of gravity G must, of course, always be below the prism-edge, otherwise the balance will be in neutral or unstable equilibrium. Makers have, therefore, a considerable choice of conditions which they can vary to obtain a given result, and we find on the market excellent "long-arm" as well as "short-arm" balances. Long-arm balances, although sensitive, possess the disadvantage of a long time of swing (10 to 15 seconds) which renders weighing with them very tedious. For moderate loads, short-arm balances constructed with light beams are much to be preferred, as they are not only sensitive, but very quick in their action. They have a time of vibration of from 6 to 10 seconds.

When the load on a balance is increased, the friction at the knife-edges increases, tending to decrease the sensibility. In addition, any elastic yielding of the beam under increased load would tend to lower the center of gravity of the beam and thus decrease the sensibility. Likewise, if the terminal knife-edges are lower than the center knife-edge, the additional load, which can be considered to be concentrated at the terminal knife-edges,

would have the effect of lowering the center of gravity of the movable parts and would thus decrease the sensibility.   If, on the other hand the terminal knife-edges are higher than the center knife-edge, the additional load would raise the center of gravity of the movable parts and would tend to increase the sensibility. The importance of this tendency, as compared to the factors tending to decrease the sensibility, will determine whether or not the sensibility will actually increase, remain constant, or decrease, in any given case.   When the terminal knife-edges are in the same plane with, or lower than the center knife-edge,
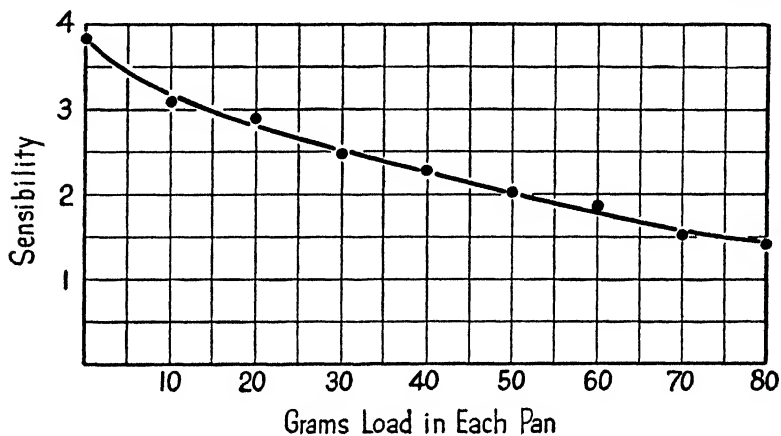
Fig. 25

Sensibility Curve of a Balance

increase in load will always have the effect of lowering the sensibility due to bending of the beam and increase of friction.   Most balances show a decreasing sensibility with increasing load, and this change of sensibility furnishes us a good criterion as to the maximum load which can be carried by the balance without injury.   The criterion is *that no greater load should ever be placed upon the balance pans than the load at which the sensibility becomes forty per cent of its maximum value.*   Thus in the case of the balance, the sensibility of which is given graphically herewith in Figure 25, no greater load than 70 g. in each pan should ever be placed upon the balance.

The sensibility of a balance can be lowered or increased by lowering or raising the gravity weight. There is a limit to the increase in sensibility which can be obtained in this way. If in raising the gravity weight, the center of gravity is made to coincide with the central knife-edge, the beam will be in neutral equilibrium; and if the center of gravity is brought up above the central knife-edge, the beam will be in unstable equilibrium. Either condition will lead to erratic results.

Before proceeding to the actual determination of the sensibility at various loads, it is necessary to determine whether or not the balance is equipped with a rider of the correct weight, because the rider must be used in determining the sensibility. This process, known as *Proving the Rider*, will be discussed in the following paragraph.

67. Proving the Rider. — The first thing to do in any case is to see that the rider is the correct one to use with the balance that has been assigned. To prove this, the 5 mg. weight from the analytical set is placed on the right-hand pan of the balance and counterpoised by placing a 5 mg. weight from an auxiliary set on the left-hand pan. The balance pans are then set swinging (§ 64) so that the extremities of the arcs to which the pointer swings lie between 0 and 5 on the left and between 15 and 20 on the right, the ivory scale of the balance being marked as represented in Figure 22. After a few oscillations of the pointer, the zero point is determined.

When this equilibrium point has been determined, the 5 mg. weight is taken off the right-hand pan and the rider is placed at division 5.0 on the right-hand beam of the balance, and the equilibrium point again determined. Obviously, if these two points are the same, then the effect of the rider when placed at division 5.0 on the beam is equal to the weight of the 5 mg. weight, and the rider is exactly right. In general the two equilibrium points will not be the same, but as long as they do not differ by more than 0.2 division (that is, for a balance having a sensibility of 2.0 to 3.0) it is all right to use the rider.

68. Determination of Sensibility of Balance. — The sensibility of a balance has been defined (§ 66) as the angle α. In practice, however, we take as a measure of this angle the number of scale

divisions displacement in the position of the equilibrium point caused by an excess of one milligram in one pan or the other. A sensibility of 2.0 to 3.0 scale divisions is suitable for weighings where a precision of 0.0001 g. is sought; as was shown in § 66 the sensibility can be increased or decreased by raising or lowering the sliding weight on the pointer of the balance; the greater the sensibility, however, the longer the time of vibration.

Details of Procedure. — The equilibrium point is first determined for empty pans. The rider is then placed at division 1.0 on the beam and the new equilibrium point determined. The difference between these two points is, by definition, the sensibility of the balance for no load in pans. In ordinary weighings it is sufficient to calculate the difference between the two equilibrium points to the first decimal place, but in the calibration of weights it will be necessary to calculate the difference to the second decimal place.

The sensibility for 10 g. load in each pan is next determined by getting the equilibrium point when there is a 10 g. weight in each pan.[4] One milligram is then added to the right-hand side by means of the rider and the new equilibrium point is obtained. From the difference of these two values we have the sensibility at 10 g. load.

In a similar manner, the sensibility must be determined for the following loads in each pan: 20 g., 30 g., 40 g., and 50 g. In order to get the sensibilities for intermediate loads, it is best to plot the results graphically, using the loads in each pan as abscissæ and the sensibilities as ordinates as illustrated in Figure 25. Such a graph should be pasted on the inside of the front cover of the laboratory notebook.

69. Direct Weighing. — In any method of direct weighing the object is placed on the left-hand pan and the weights on the right. Due to inequalities in the lengths of the balance-arms, the masses obtained by this method are strictly not the true masses but are proportional to them, and hence give a correct value for the ratio of the masses. In those quantitative processes

[4] If the weight from the analytical set and that from the auxiliary set happen to be so unequal that the pointer swings off the scale, small fractional weights should be added to one pan or the other as the case may be.

in which we are concerned with a ratio of masses, direct methods of weighing find wide application.

70. Direct Weighing Using Sensibility. — In this method of weighing we must first determine the zero point of the balance with empty pans. Then, after making sure that the beam arrests and pan supports are up, the object is placed on the left-hand pan. Beginning with the largest integral weight of the set, we surmise which is the first weight, as we go downward in the scale, that will establish an inequality of weight in favor of the object, *i.e.*, which is the largest single weight that will not over-balance the object. This weight is placed on the pan, and the beam arrests partially lowered to show whether the weight is too heavy or not. Upon the assumption that it is not too heavy, the beam arrests are raised, and the next weight of the set in order of descension is added, the beam arrests are partially lowered again to show the inequality and then are raised. If this weight is too heavy, it is removed and the next lower weight substituted for it; if it is not too heavy, it is left on the pan and the next lower weight tried in addition, and so on down the set in regular manner to the one-gram weight, it being always remembered to raise the beam arrests before the addition or removal of any integral weight. During the process of adjusting the integral weights, the pan supports are always kept up. When the frac-tional weights are reached, the beam arrests are kept completely lowered but the pan supports are kept up during the addition or removal of a fractional weight and only released to show the inequality. The fractional weights are likewise added systemati-cally in order of descension down to and including the five-milli-gram weight.

The adjustment to the nearest milligram is now made by means of the "rider." As already mentioned in § 62, this accessory is a small piece of platinum wire which is placed upon the beam of the balance, usually the right beam. The actual weight of a rider for giving milligrams should be the same number of milli-grams as the number of whole divisions into which the beam is actually or constructively divided between the central prism-edge and the terminal prism-edge. Thus if the beam is divided into six whole divisions, a six-milligram rider should be used,

because, from the principle of moments, such a rider, if placed at division one on the beam, will produce an effect equal to 1 mg. in the pan; if placed at division two, it will produce an effect equal to 2 mg. in the pan, etc. Owing to the different calibration of balance beams and the different weights of riders, every rider should first be proved before it is accepted for use (*cf.* § 67).

It is not practicable to obtain the nearest tenth of a milligram by placing the rider at successive fractional divisions on the beam and noting the displacements of the needle upon releasing the pan supports, because, even with the most careful final adjustments of the rider and with the utmost care in releasing the pan supports, the needle will persist in swinging through a small arc which corresponds to several tenths of a milligram. Recourse is consequently had to the procedure known as the "method of swings" which is not only very simple but also time-saving. In this method the rider is adjusted to the nearest milligram, the pan supports are lowered and the zero point for loaded pans is determined. The difference between this zero point and the zero point for empty pans, divided by the sensibility for the given load, gives the fraction of a milligram to be added or subtracted from the weights on the pan inclusive of the rider. An illustration of the weighing of a platinum crucible by the balance mentioned in § 66 will make this clear.

Zero point with empty pans   10.2
Zero point when crucible was counterbalanced by 22.487 g. 11.7
Difference in zero points (displacement being to the right)   1.5
Sensibility for this balance for load of 22 g. is 2.8 (§ 66)
∴ correction is 1.5 ÷ 2.8 = 0.5 mg. which must be added because the weights were too light.

As soon as the zero point for loaded pans has been determined, the balance is stopped swinging by bringing up the pan supports when the needle is passing by the middle point of the scale. The beam arrests are then immediately raised so as to take the load off the prism-edges.

The weight of the object or substance should be recorded, first, by adding up the weights missing from the box (in which count every weight should have its own place) and, second, by

checking them off as they are returned to the box. This procedure gives a check which is most desirable, as it happens more often than would be supposed that the first count was incorrectly made. In placing weights on the balance pan, some systematic arrangement should be used in order to facilitate the counting of the weights.

71. *Direct Weighing Using One Short Swing.* — When a high degree of precision is not required, time may often be saved by using a method of weighing which is the same as the one just described, except for the fact that only one reading is taken at each extremity of a single swing of the pointer, and except for the fact that this swing is much shorter than is usual in the previous method. In this method [5] the swing is usually over an arc measured by eight scale divisions or less. When the swing is small, the decrement due to damping is small and is neglected. The average of the readings taken at the extremities of the single swing is assumed to be the zero point.

72. *Direct Weighing Without Using the Sensibility of the Balance.* — The first step in this method is to determine the zero point of the balance. The second step is to place the object on the left-hand pan and balance it with weights on the right. The rider is then used to obtain the tenths of a milligram by shifting it until the pointer swings equal distances on both sides of the zero point. This method makes it unnecessary to know the sensibility of the balance. However, much time is often required to exactly counterbalance the object, and, if the object has the tendency of gaining or losing weight while being weighed, a considerable error may be introduced from this source.

When it is required to weigh out a definite weight of a sample, a modification of this method can be used. The required weights are placed on the balance, and the sample is added until the pointer swings equal distances on both sides of the zero point. The sample, of course, should never be added directly to the pan. Balanced watch-glasses or some other form of counterpoised container should be used.

73. *Direct Weighing by Single Deflection.* — In this method the center of gravity of the beam of the balance is displaced

[5] H. L. Wells, *J. Am. Chem. Soc.,* **42,** 411 (1920).

to the left by means of the adjusting screw on the beam, shown at
Y in Figure 22. The adjusting screw is turned until, on releasing
the beam and the pans, the pointer swings to the right to some
point between 13 and 17 on the scale. This point is then taken
as the point of reference in the subsequent weighing. In the
actual weighing, the object is placed on the left-hand pan and
balanced with weights until the pointer on its first swing is de-
flected to the right as far as the point of reference. This method
necessitates using the rider to obtain the tenths of a milligram
and, consequently, may not be suitable in weighing samples
which tend to change weight rapidly. This method does not
require that the sensibility of the balance be known. Before
this method can be used with any degree of assurance of obtaining
reliable results, it should be thoroughly tested with known weights
on the same balance which is to be used in the actual weighing.

74. Errors of Weighing. — The chief errors that may occur
in weighing are those due to the following causes:

1. Inequality of the lengths of the balance-arms.
2. The buoyant effect of the air.
3. Changes in composition of substance during weighing.
4. Changes in the condition of the container.
5. Inaccuracy of the weights.

These sources of error will be discussed in the order given.

75. Inequality of Length of Balance-arms. — Since the length
of the two arms of a balance are never equal, it is evident that an
object will apparently have different weights according to whether
it is placed in the left-hand or in the right-hand balance-pan. As
it can be shown that the true weight lies between these two appar-
ent values, it follows that every "direct weighing" is attended
with a certain error. Whether this error is allowable depends
upon its magnitude and the accuracy which is being sought. In
a good analytical balance the relative lengths of the arms seldom
differ by more than one part in 40,000, but in many of the cheaper
balances the difference is much greater than this.

It might be thought that, whatever the ratio of the relative
lengths might be, it could be determined at the start, and then
used as a factor to correct subsequent weighings. This procedure,
however, is not valid because the ratio is not a constant quantity,

but varies from time to time on account of temperature changes inside the balance case, or, indeed, it may acquire an entirely different value due to a displacement of a prism-edge through accident or jarring. For the former reason a balance should be protected from direct sunlight and from all hot and cold draughts of air. Moreover, any object to be placed on the balance-pans should be at, or very near to, the same temperature as obtains inside the balance case. For the latter reason a balance should be protected from jarring or vibration, and the prism-edges always brought down very gently upon the agate planes.

With reference to the accuracy being sought, it must be emphasized that whenever the element of absolute value enters into the determination in any way, either directly or indirectly, it is necessary to eliminate the error introduced by the inequality of the balance-arms. This elimination can be accomplished by either of the two methods to be described presently: (1) Borda's method of substitution, (2) Gauss's method of double weighing.

As an illustration to show where the element of absolute value enters into a determination, let us consider the calibration of a piece of volumetric apparatus. The weight of water contained by the piece of volumetric apparatus is corrected to eliminate the error due to the buoyant effect of the air. The capacity is determined by dividing this corrected weight of water W by the corrected weight of 1 ml. of water w at the same temperature. The values for w have been determined once and for all in terms of the absolute unit, and they are so given in the tables. It therefore becomes obvious that if the water has been weighed by a "direct weighing," the recorded weight, when corrected for the buoyant effect of the air, will contain the error due to the inequality of the balance-arms. Let us represent this value by W'. It follows that the ratio W': w will not represent the true capacity.

In those determinations where merely a ratio of weights is sought, as in the determination of the percentage of a constituent in a given substance, it is allowable to make direct weighings if the substances which are weighed are always placed in the same pan, usually the left-hand one. By this procedure, the effect due to the inequality of the balance-arms is either eliminated or becomes negligible, as shown in the following discussion.

For convenience, suppose, during the first weighing, the right arm to be longer than the left arm in the ratio $R:L$, and let M be the mass of the substance used for analysis; suppose during the second weighing the ratio to be $R':L'$ and let m be the mass of the precipitate found. Then $M\dfrac{L}{R}$ and $m\dfrac{L'}{R'}$ will be the corresponding apparent weights, namely, the weights as recorded. We see at once that

$$\frac{m\dfrac{L'}{R'}}{M\dfrac{L}{R}} = \frac{m}{M}$$

provided that $\dfrac{L'}{R'} = \dfrac{L}{R}$, or, in other words, provided that the ratio of the relative lengths of the arms has been the same during the two weighings.

For a good balance having proper usage and care, the difference between $\dfrac{L'}{R'}$ and $\dfrac{L}{R}$ will be very small indeed in the case of consecutive weighings which are made, one soon after the other. Under these conditions, it follows that the ratio represented by the left-hand member of the above inequality approximates so very closely to the value of the right-hand member that, for all purposes where direct weighings are allowable, we can consider the two sides of the inequality as equal.

If the weighings are made on a faulty balance, or if one of the balance-arms has been exposed to a higher temperature than the other through the weighing of a hot crucible or exposure to sunlight, the difference between $\dfrac{L'}{R'}$ and $\dfrac{L}{R}$ may be large enough to invalidate our considering the ratio of the apparent weights as equal to the ratio of the masses.

76. Borda's Method of Substitution. — According to this method, the object, whose mass is M, is placed in the right-hand pan of the balance and counterbalanced or tared by the necessary weight T, which may be lead shot, or preferably the weights of a duplicate set. Then the object is removed and the necessary weights put on in its place to counterbalance the counterpoise.

We have from the first weighing

$$TL = MR,$$

and from the second weighing

$$TL = WR.$$

Dividing the first equation by the second, we see that

$$\frac{M}{W} = 1 \quad \text{or} \quad M = W. \tag{6}$$

We therefore conclude that the weight of the object being weighed is equal to the weights which were substituted for it on the right-hand pan.

77. Gauss's Method of Double Weighing. — In this method the object is first placed in one pan and the weights in the other and a weighing is made. The object and weights are then interchanged on the respective pans, and a second weighing is made. These two weighings are then used to compute either the geometric mean or the arithmetic mean.

If an object, whose true mass is M, is placed upon the left-hand balance-pan and is counterbalanced by weights W on the right-hand pan, we have by the principle of the lever-arm

$$ML = RW. \tag{1}$$

If now the object is placed in the right-hand pan and is counterbalanced by weights W' on the left-hand pan, we have

$$MR = LW'. \tag{2}$$

Upon multiplying the first equation by the second and canceling out the common factor RL, we get

$$M^2 = WW' \quad \text{or} \quad M = \sqrt{WW'}. \tag{3}$$

That is to say, the mass is equal to the square root of the product of the apparent weights.

For most purposes, however, it is sufficiently accurate to take the average of the apparent weights

$$M' = \frac{W + W'}{2} \tag{4}$$

if the two weights W and W' do not differ very much from each other.

The validity of using the average is justified as follows. Let the difference between the apparent weights be a. Then $W' = W \pm a$ according as W' is greater than or less than W. Whence from (3) we have

$$M = \sqrt{W(W \pm a)} = \sqrt{W^2 \pm Wa}.$$

Now

$$\sqrt{W^2 \pm Wa} = W \pm \frac{a}{2} \mp \frac{a^2}{8W} \pm \frac{a^3}{16W^2} \mp \frac{5a^4}{128W^3} \pm \cdots$$

Since this is an alternating series, the value of the remainder after n terms is numerically less than the value of the $(n + 1)$st term. If we include only the first two terms, $W + \frac{a}{2}$ then the value of the sum of all the succeeding terms is less than $\frac{a^2}{8W}$. That is to say, the value of M is represented by $W + \frac{a}{2}$ with a difference not greater than $\frac{a^2}{8W}$. But $W + \frac{a}{2}$ is the same as $\frac{W + W + a}{2}$ or $\frac{W + W'}{2}$, whence we establish the proposition that M is the same as $\frac{W + W'}{2}$ except for a difference not greater than $\frac{a^2}{8W}$, and since for our ordinary analytical balances a is so very small in comparison with W, the difference is negligible.

Comparing the two methods, Gauss's and Borda's, it may be mentioned here that, other things being equal, the probable error of Gauss's method is less than that of Borda's. For problems involving the determination of only a few absolute weights, Gauss's method is probably to be preferred, but in the calibration of weights which involve quite a number of determinations, Borda's method lends itself far more readily to the problem.

78. Determination of the Ratio of the Lengths of the Balance-arms. — If we divide equation (2) of §77 by (1) and solve for $\frac{R}{L}$, we get $\frac{R}{L} = \sqrt{\frac{W'}{W}}$. The quantity under the radical sign can be developed in terms of a series of powers of a and W, whereas

before a represents the difference between W' and W, *i.e.*, $W' = W \pm a$. Thus,

$$\frac{R}{L} = 1 \pm \frac{a}{2W} \mp \frac{a^2}{4W^2} + \cdots$$

Discarding terms of a higher order than the first, we get

$$\frac{R}{L} = 1 \pm \frac{a}{2W},$$

the upper sign being used when W' is greater than W, and the lower sign being used when W' is less than W.

79. Buoyant Effect of the Air. — According to Archimedes' Principle an object totally immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. When a weighing is made in air, both the object and the weights are totally immersed in the fluid, air. Consequently, in addition to the gravitational forces acting downward on both object and weights, we have buoyant forces acting upward on each. Figure 26 illustrates the balancing of a sample of an alloy having a density of 4.00 g. per ml. and a volume of 12.50 ml. by means of a 50.0000 g. brass weight having a density of 8.40 g. per ml. and a volume of 5.95 ml., the weighing being done in air having a density of 0.0012 g. per ml. W_v and W_a represent the forces of gravity acting downward on the object and the weight, respectively. The buoyant force B of the air on the object is 12.50×0.0012 or 0.0150 g. while the buoyant force B' of the air on the brass weight

Fig. 26

Forces Involved in Weighing Carried Out in Air

is only 5.95×0.0012 or 0.0071 g. Since B is larger than B' and since the balance is in equilibrium, it follows that W_v must be greater than W_a. Now let us suppose that the balance has

an air-tight case, from which practically all the air is pumped, thereby producing a vacuum inside.   This would be equivalent to removing a supporting force of 0.0150 g. from the left-hand pan and a supporting force of 0.0071 g. from the right-hand pan. Obviously, since W_v is greater than W_a, the left-hand pan will move downward, the right-hand pan will move upward and the pointer will swing to the right.   To restore equilibrium, additional weight will have to be added to the right-hand pan.   The weight needed will be the difference between the two buoyant forces which were removed from the two pans when the vacuum was created, or $0.0150 - 0.0071 = 0.0079$ g. is the weight required. It is seen then that the weight W_v of the object in a vacuum is 50.0000 g. $+$ 0.0079 g. or 50.0079 g.

If the object and weights have the same density, they will also have the same volume and the buoyant forces will be equal and need not be considered.   Under these conditions the weight of the object in air will be the same as its weight "in vacuo." If the density of the object is greater than that of the weights, then the weight in air will be greater than the weight "in vacuo."

It would be impracticable in ordinary procedure to evacuate the balance case while making a weighing.   Hence it is necessary to be able to calculate, from the weight of an object in air, what it would have weighed had it been weighed in a vacuum. The method of correcting to "in vacuo" will now be discussed.

80. Correction for Buoyant Effect or Reduction of Weighings to "in Vacuo." — On account of the difficulty of making weighings in a vacuum, it is customary to make the weighings in air and then correct for the buoyant effect of the air in the manner already illustrated.   In the illustration given the weight "in vacuo" W_v of the object was obtained from the "in vacuo" value of the weights used in making the weighing in air, W_a, by adding the weight of air B displaced by the object and subtracting the weight of air B' displaced by the weights.   Thus,

$$W_v = W_a + B - B'.$$

Let V and V' represent the volumes of object and weights respectively, and D and D' the corresponding densities.   Also let S represent the density of the air.

Then $$B = VS \tag{1}$$

and $$B' = V'S \tag{2}$$

whence $$W_v = W_a + VS - V'S. \tag{3}$$

Since $$V = \frac{W_v}{D} \tag{4}$$

and $$V' = \frac{W_a}{D'} \tag{5}$$

where W_a is the "in vacuo" value of the weights used to make the weighing in air, it follows that

$$W_v = W_a + \frac{W_v S}{D} - \frac{W_a S}{D'} \tag{6}$$

and

$$W_v - \frac{W_v S}{D} = W_a - \frac{W_a S}{D'} \tag{7}$$

whence

$$W_v \left(1 - \frac{S}{D}\right) = W_a \left(1 - \frac{S}{D'}\right); \tag{8}$$

therefore $$W_v = W_a \frac{\left(1 - \dfrac{S}{D'}\right)}{\left(1 - \dfrac{S}{D}\right)}. \tag{9}$$

When the difference between the density of the weights and object is very small and therefore the difference between W_v and W_a is very small, a method of approximation may be used to give substantially correct results. In this method W_v on the right-hand side of equation (6) is replaced by W_a. It follows that

$$W_v = W_a + \frac{W_a S}{D} - \frac{W_a S}{D'}.$$

81. Calculation of Weight in Air from Weight "in Vacuo." — It follows from equation (9) that

$$W_a = W_v \frac{\left(1 - \dfrac{S}{D}\right)}{\left(1 - \dfrac{S}{D'}\right)}.$$

When the difference between W_v and W_a is very small, the equation

$$W_a = W_v + \frac{W_vS}{D'} - \frac{W_vS}{D}$$

may be used.

To illustrate the application of this equation, let us calculate the weight of a liter of water in air when weighed with brass weights at 20° and 760 mm. from its weight "in vacuo." Referring to Table 8, it is seen that the weight "in vacuo" is 998.23 g.

Table 8

WEIGHT "IN VACUO" OF 1 ML. OF WATER

(Quoting from: Landolt-Börnstein, p. 74 of reference given in § 11; according to measurements of Thiesen, Scheel and Disselhorst. *Wiss. Abhandl. physik. tech. Reichsanstalt.*, **3**, 68 (1900).)

Temp. °C.	Grams	Temp. °C.	Grams
0	0.99987	19	0.99843
1	0.99993	20	0.99823
2	0.99997	21	0.99802
3	0.99999	22	0.99780
4	1.00000	23	0.99756
5	0.99999	24	0.99732
6	0.99997	25	0.99707
7	0.99993	26	0.99681
8	0.99988	27	0.99654
9	0.99981	28	0.99626
10	0.99973	29	0.99597
11	0.99963	30	0.99567
12	0.99952	40	0.99224
13	0.99940	50	0.98807
14	0.99927	60	0.98324
15	0.99913	70	0.97781
16	0.99897	80	˙0.97183
17	0.99880	90	0.96534
18	0.99862	100	0.95838

If the flask containing the water were tared by an exactly similar flask so as to compensate for the buoyant force on the flask alone, and 998.23 g. of brass weights were added to the opposite pan, it would be found that the weight added is too heavy. We shall now calculate the weight which should be added to establish

equilibrium in air. Consulting Table 9, we find the buoyant effect of the air upon the water is

$$\frac{W_vS}{D} = \frac{998.23 \times 0.0012}{0.99823} = 1.20 \text{ g.}$$

because this is the weight of the liter of air displaced by the water. The buoyant effect of the air on the brass weights is the volume of the weights multiplied by the weight of 1 ml. of air at 20° and 760 mm. This is approximately

$$\frac{W_vS}{D'} = \frac{998.23 \times 0.0012}{8.4} = 0.14 \text{ g.}$$

Therefore, the net amount by which the 998.23 g. is too heavy is $1.20 - 0.14 = 1.06$ g. We obtain, therefore, as the weight of one liter of water under the conditions stated,

$$998.23 - 1.06 = 997.17 \text{ g.}$$

82. Effects of Temperature, Pressure, and Humidity on Buoyancy of Air. — Since the correction for the buoyant effect of the air depends upon the weight of the displaced air, and the weight of the displaced air in turn depends upon the temperature, pressure, and humidity existing at the time of the weighing, it becomes necessary to inquire into the effect of these factors.

In regard to temperature and pressure, we have from the well-known gas law, $PV = RT$, that the weight of a given volume of air varies inversely as the absolute temperature and directly as the pressure, whence from the data of Leduc and of Rayleigh[6] we are able to derive the formula for the density of dry air:

$$d = \frac{0.0012928}{1 + 0.003670\,t} \cdot \frac{H}{760}$$

where d is the weight in grams of 1 ml. of dry air; t is the temperature of the air; H is the height of the barometer column in

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[6] 0.0012928 is the average of the measurements of A. Leduc, *Ann. chim. phys.* (7) **15**, 26 (1898), and Lord Rayleigh, *Proc. Roy. Soc.*, **53**, 147 (1893) as given in Landolt-Börnstein, "Physikalisch-Chemische Tabellen." See reference given in § 11.

millimeters of mercury.   The application of this formula gives
us the values in Table 9.

Table 9

WEIGHT OF ONE LITER OF DRY AIR IN GRAMS

Temp.	Barometric Pressure mm. Hg.			
	720	740	760	780
0°	1.225	1.259	1.293	1.327
10	1.181	1.214	1.247	1.280
15	1.161	1.193	1.225	1.258
20	1.141	1.173	1.204	1.236
25	1.122	1.153	1.184	1.215
30	1.103	1.134	1.164	1.195
35	1.086	1.116	1.146	1.176

In regard to humidity, the air may contain: (1) no moisture,
in which case it is called dry air; (2) the maximum amount of
moisture corresponding to the given temperature, in which case
it is called moist saturated air; (3) an amount of moisture some-
where in between (1) and (2).

As (1) and (2) are limiting values of (3) and we have already
obtained the values for (1), we will now obtain them for (2).   The
density of moist saturated air is given by the formula

$$d = \frac{0.0012928}{1 + 0.003670\,t} \cdot \frac{H - \frac{3}{8}h}{760},$$

where d, t, and H have the same significance as before and h
represents the maximum partial pressure, in millimeters of mercury,
of the water vapor that can exist in the air at the given tem-
perature.   The values of h are as follows:[7]

Temp. °C.	0	10	15	20	25	30	35
Value of h	4.6	9.2	12.8	17.5	23.8	31.8	42.2

[7] Landolt-Börnstein, p. 360, 1912, quoting from Scheel and Heuse, *Ann. der
Physik.* (4), **31**, pp. 715–736 (1910).

Table 10 gives the weight in grams of one liter of saturated air at a variety of temperatures and pressures.

Table 10

WEIGHT OF ONE LITER OF MOIST SATURATED AIR IN GRAMS

Temp.	Barometric Pressure mm. Hg.			
	720	740	760	780
0°	1.222	1.256	1.290	1.324
10	1.176	1.209	1.241	1.274
15	1.153	1.185	1.217	1.250
20	1.131	1.163	1.194	1.226
25	1.108	1.139	1.170	1.201
30	1.085	1.116	1.146	1.177
35	1.062	1.092	1.122	1.152

Now under actual working conditions of laboratories, for altitudes not over 300 meters, it is not likely that we would have air lighter than that corresponding to moist saturated air for 30° and 720 mm., nor heavier than that corresponding to dry air for 15° and 780 mm., namely, no lighter than 0.00108 g. per ml. nor heavier than 0.00125 g. per ml. Therefore, for most purposes of correction, it will be satisfactory to assume the weight of 1 ml. of air as equal to 0.0012 g.

83. *Procedures Requiring Correction to "in Vacuo."* — Strictly speaking, the mass of an object is its mass "in vacuo" and, where absolute values are being determined, or where the element of absolute values enters into a ratio, it is necessary to refer weighings to this standard. For most analytical purposes, however, where the intention is to obtain the result in terms of percentage, the ratio of the weights in air, as far as solids are concerned, will give a value which is sensibly the same as that which would be given by the weights "in vacuo."

In regard to liquids, it depends largely upon the purpose of the weighing as to whether weights "in vacuo" must be used or whether weights in air are allowable. The weights "in vacuo" must be used in determining, for purposes of calibration, the amount of water contained or delivered by a piece of volumetric

apparatus. In the determination of the specific gravity of a material, the weights in air will suffice, since specific gravity is defined as the ratio of the weight of a given volume of substance to the weight of the same volume of water, the temperature of each at the time of weighing being given. However, if the density is desired, the weights "in vacuo" must be used. No ratio is involved here, for density is merely the mass of substance per unit volume. In terms of the c.g.s., or absolute units, it is the grams of substance per milliliter.

Concerning gases, whenever it is necessary to weigh these, as for instance in Dumas' method [8] for the determination of molecular weight, the weights "in vacuo" are alone permissible because of the enormous error that would be introduced by employing the weights in air.

The buoyant effect of the air must be considered in the construction of a set of analytical weights for weighing in air. Let us suppose that the fractional weights are made of platinum having a density of 21.4 g. per ml.; while the weights of 1 g. and larger are made of brass having a density of 8.4 g. per ml. If the whole set were constructed of brass, it would possess consistency throughout as far as the buoyant effect of the air is concerned. A platinum fractional weight, however, would have a smaller volume than a brass weight of the same mass, would be buoyed up with a smaller force and, hence, would produce a greater net downward force than would the brass. In order to bring about consistency, it is necessary to decrease the masses of the platinum weights so that they will produce the same effect on the balance as the corresponding brass fractional weights. Similar adjustments must be made for fractional weights of other metals differing in density from brass.

84. Change in the Composition or Weight of a Substance during Weighing. — A change in weight during weighing is likely to occur in the case of hygroscopic, efflorescent or volatile substances, or substances which absorb carbon dioxide or oxygen. In order to obviate this difficulty of change of weight during

[8] For a brief account of Dumas' method, see Kipping and Kipping, "Perkin & Kipping's Organic Chemistry." Part I, 5th ed., p. 21, J. B. Lippincott Co., Philadelphia, 1936.

weighing, use is made of closed vessels, such as the various types of weighing bottles,[9] tubes,[10] or pipettes [11] or, in the case of ignited or dried precipitates, the containing crucible is weighed with its cover on.

The ordinary form of weighing bottle with the ground-in glass stopper is objectionable for weighing powders because small particles adhere very easily to the ground surface of the bottle, and when the stopper is firmly pressed into place, they either tend to bind the stopper or else are forced out and slide off the bottle. In order to overcome this, Mangold [12] has devised a special form of stopper, while F. L. Guttmann [13] has replaced the ordinary ground-in stopper by a ground-on cap, an improvement which is particularly advantageous in weighing out successive portions of a hygroscopic substance or of liquids. Guttmann in the article referred to also describes a weighing bottle with ground-in tubes for use in drying substances to constant weight in a current of gas, as in the determination of water of crystallization, etc.

When it comes to weighing ignited precipitates, the practice of using covered crucibles is to be recommended for the reasons given in § 28. Moreover, it is not possible to weigh certain ignited precipitates such as aluminum oxide, calcium oxide,[14] etc., which rapidly absorb constituents normally present in the atmosphere, unless the containing crucible is covered. In these cases it is a good plan to make a first weighing, then to repeat the ignition and cooling, and, before taking the crucible out of the desiccator,

[9] Weighing bottles with pipette stoppers for weighing out liquids are described by Levi, *J. Am. Chem. Soc.*, **27**, 614 (1905).

[10] For weighing tubes with two legs to prevent rolling, see Gawalovski, *Chem. Zentr.* (3), **16**, 369 (1886).

[11] For pipettes for weighing corrosive liquids, see Berl, *Chem.-Ztg.* **34**, 428 (1910); Lunge & Rey, *Z. angew. Chem.* **4**, 702 (1891); Rosenlecher, *Z. anal. Chem.* **37**, 209 (1898).

For pipettes for weighing liquids which spoil on exposure to the air, see D. Holde, *Z. angew. Chem.* **12**, 711 (1899); H. Schweitzer, *J. Am. Chem. Soc.* **15**, 190 (1893); E. Reichard, *Z. anal. Chem.* **7**, 187 (1868).

[12] C. Mangold, *Z. angew. Chem.* **4**, 441 (1891).

[13] F. L. Guttmann, *J. Am. Chem. Soc.*, **28**, 1667 (1906).

[14] *Cf.* W. F. Hillebrand, *Bulletin* 422, U. S. Geological Survey, p. 119, 1910, "The lime should not be left over half an hour in the desiccator before weighing, for it gains weight appreciably if left long."

to place the necessary weights on the balance-pan; in this way a third weighing will usually suffice to check the second.

As already mentioned in § 64, the efficacy of keeping a dish of concentrated sulfuric acid or of granulated anhydrous calcium chloride in the balance case, for the purpose of retarding the absorption of moisture by the precipitate while being weighed, has been shown by O. Kuhn [15] to be worthless. It therefore seems best to have no dehydrating agent in the balance case, but in accordance with the recommendation of Ostwald,[16] to make a weighing as rapidly as possible after removing an object or substance from the desiccator.

85. Change in the Condition of the Container. — In a great many analytical determinations, the weight of substance used or found is obtained by difference; that is, the weight of the container is subtracted from the joint weight of the container and the substance. This method of arriving at the weight of the substance presupposes that the weight of the container remains constant during the operation throughout which it is used. There are, however, certain influences which may cause the container to change in weight during its use, namely, condensation of moisture from the atmosphere, electrification due to wiping, replacement of the air in the container by some other gas, loss in weight due to ignition.

86. *Condensation of Moisture from the Atmosphere.* — Many materials exhibit the property of collecting a film of moisture on their exposed surface when allowed to stand around in air which contains water vapor. This phenomenon seems to be associated with the specific nature of the material, because glass and porcelain are particularly subject to it, while polished or lacquered metals are affected to only a very slight extent. In addition to the specific nature of the material, there are other contributing factors which influence the amount of surface-moisture that is collected, namely, the dryness of the object to begin with, the area of the exposed surface, the humidity of the air, and the time of exposure. From these considerations it follows that, for any object, the

[15] O. Kuhn, *Chem.-Ztg.*, **34**, 1097–1108 (1910).
[16] W. Ostwald and R. Luther, "Hand- und Hilfsbuch zur Ausführung physiko-chemischer. Messungen," W. Engelman, 5th ed., Leipzig, 1931.

amount of surface-moisture is not a constant quantity but a variable. In order to minimize the error which is introduced in weighing by virtue of this fact, recourse is always had to some procedure that will reduce the surface-moisture to the lowest amount that is practicable and that will be sensibly duplicated for all the weighings which have to be made with the container during the operation. The most effective way of reducing surface-moisture is by heating the container to a high temperature. Thus, in the case of a crucible which is to be subsequently used in the ignition of a precipitate, it is first submitted to a preliminary ignition without the precipitate so that its weight "empty" shall be as free from surface-moisture as its weight when weighed with the precipitate. If the container cannot be heated but must stand in the air during its use, as is the case with watch-glasses or with absorption bulbs used in the determination of carbon dioxide, the surface-moisture must be reduced as much as possible each time before a weighing is made by *very gently* wiping the object with a piece of old soft linen, surgical gauze, or lens paper (never with silk). This method largely removes the surface-moisture but, unfortunately, generates more or less of a static charge of electricity which interferes with the weighing as discussed in the next paragraph.

87. Electrification Due to Wiping. — While the static charge of electricity generated has no measurable weight, it acts as though it had when the container is placed on the balance-pan because of the torque effect which the attractive (or repulsive) force of the charge produces on the balance-pan. For glass objects presenting an area of about 150 sq. cm., the static charge ordinarily produced may exert a force equivalent to 100 milligrams or more right after the wiping.[17] As successive wipings of the same object do not necessarily produce the same sized charge, it is evident that if an object is weighed immediately after wiping, successive weighings will be affected by an indeterminate error due to the presence of the static charge. In order to reduce this error, advantage can be taken of the fact that these charges become less and less upon standing, but meanwhile, however, the surface-moisture

[17] H. K. Miller, "Electrical Disturbance in Weighing," *J. Am. Chem. Soc.*, **20,** 428 (1898).

will be accumulating so that the question arises as to how much time must elapse after wiping in order that the resultant error due to the two disturbances shall be sensibly constant. The proper time seems to be about ten minutes for small glass objects, because in this period the charge will have largely dissipated itself, and this means that for consecutive weighings, the variation in the effect due to the remaining portion of the charge will be very slight. Moreover, in this same period the variation in the amount of surface-moisture that will collect will also be very slight, provided that the humidity has not changed materially between consecutive weighings. · If, therefore, consecutive weighings (preceded of course by the wiping and standing for ten minutes) are made closely enough together so that the humidity shall not have undergone much change, we may reasonably assume that the resultant error, due to the static charge and the surface-moisture, is sensibly constant and hence disappears in the subtraction by which we arrive at the weight of the substance.

88. Replacement of the Air in the Container by Some Other Gas. — Whenever it is necessary to determine the element carbon, the carbon is burned in a stream of oxygen, and the resulting carbon dioxide and excess of oxygen is passed through a column of soda lime contained in some form of absorption bulb. At the end of the combustion, the gaseous region in the absorption bulb will be filled with oxygen. If at the start it was filled with air, it is evident that a change of weight has been brought about by the replacement of the air by the oxygen. In order to gain an idea of the amount of this change, let us consider that we have been using a U-tube as an absorption bulb and that 40 ml. of air has been replaced by oxygen. We know that 1 liter of saturated air at 20° and 760 mm. total pressure weighs 1.194 g. while 1 liter of oxygen under similar conditions weighs 1.331 g., from which it is easily seen that the difference in weight brought about by the replacement of the 40 ml. of air by oxygen in the above case is 0.0055 g. Upon the basis that the weight of the absorbed carbon dioxide is usually between 0.080 and 0.100 g., it follows that 0.0055 g. represents an error of 69 to 55 parts per 1,000.

89. Loss in Weight of Container due to Ignition. — Loss ·in weight occurs in the case of platinum crucibles when they are

subjected to strong ignition, because, at temperatures over 900°, platinum and iridium, which is often alloyed with platinum, are appreciably volatile, as shown by several investigators.[18] The results obtained by Burgess and Waltenberg are given in Table 11.

Table 11

APPROXIMATE LOSS IN WEIGHT, MG./100 CM.^{2}/HOUR, AT TEMPERATURE
INDICATED, FOR PLATINUM NEARLY FREE FROM IRON

Platinum Containing	Pure Pt	1% Ir	2.5% Ir	8% Rh
900° C or less	0	0	0	0
1,000	0.08	0.30	0.57	0.07
1,200	0.81	1.2	2.5	0.54

At temperatures higher than 1,200°, the loss would be still greater, so that when a blast lamp or a Meker burner is used, and the temperature is about 1,400°, the loss in weight of an ordinary sized platinum crucible (one having a volume of 25 ml. and an area of 80 cm.^{2}) may amount to several milligrams per hour.

In consequence of this behavior, it is necessary, when the weight of the precipitate is to be determined by difference, to make a correction.   This should be done, as pointed out by Hillebrand,[19] in either of two ways: the rate of loss should be determined from time to time and allowance made accordingly, or else the weight of the crucible should be taken after, and not before, ignition of the precipitate.

90. Inaccuracy of the Weights. — Since the individual weights of even a good set of weights often differ by as much as several tenths of a milligram from the denomination with which they are marked, it becomes necessary, as mentioned in § 62, to determine the values of the weights and to construct a table accordingly.

[18] Burgess and Waltenberg, *Ind. Eng. Chem.*, **8**, 487 (1916); Burgess and Sale, *ibid.*, **6**, 452 (1914); **7**, 561 (1915); R. W. Hall, *ibid.*, **22**, 494 (1900); G. A. Hulett and C. W. Berger, *ibid.*, **26**, 1512 (1904).

[19] W. F. Hillebrand, p. 102, reference given in § 11.

This operation, which is known as the calibration of weights, is described in detail in § 91.

The values of the weights can be determined, (1) in terms of the one gram weight of the set or, (2) more preferably, in terms of some standard weight which has been standardized by the Bureau of Standards at Washington.

If the values are determined according to (1), their use is limited to those determinations where the element of absolute value does not enter into the result in any way, or practically to those cases where the result can be obtained as the ratio of relative weights. Thus in the determination of the percentage of a constituent in a substance, since the percentage is one hundred times the ratio of the weight of substance found to the weight of substance used, it is immaterial in what unit the two weights are expressed, provided that the same unit is used throughout. If the values are determined according to (2), they can be used in every case in place of (1) and, furthermore, in all cases where the element of absolute value *does affect* the final result. From what has just been said and from the fact that it is relatively a simple matter to obtain (2) from (1), it is obvious that the values under (2) are really the only ones that should be used in analytical work.

We have already given one illustration in § 75 in which the element of absolute value enters into the determination. As another illustration, let us consider the preparation and use of standard solutions where it is desired to express the concentration of the reagent either in terms of molarity or normality. Since the former is the number of gram-formula weights, or moles, of the substance per liter of solution, while the latter is the number of gram equivalents of the substance per liter of solution, it is evident that the weights of the substance used must be known in terms of the standard gram or absolute unit, if a strict meaning is to attach to the compound units, molarity and normality.

91. Calibration of Weights.[20] — The purpose, in this exercise, is to determine the values of the various weights in the analytical

[20] For a description of other methods of calibrating weights see T. W. Richards, *J. Am. Chem. Soc.*, **22**, 144 (1900); or J. C. Olsen, "Quantitative Chemical Analysis," 5th ed., p. 16 of reference given in § 11; or *Nat. Bur. Standards, Circular* No. 3 of reference given in § 60.

set of weights so that we may be sure of these values to within one-tenth of a milligram. In brief, the principle involved is this: We first ascribe an arbitrary value of five units to the 5 mg. weight and then determine the values of the other denominations in terms of this arbitrary unit. Having thus determined the relative values of the various weights, we get their absolute values by ascertaining the absolute value of one of the heavier weights of the set, and, from this and the relative values, computing the absolute values of the other weights. The actual work in arriving at this determination consists essentially of the four following steps:

1. Proving the rider.
2. Determination of the sensibility of the balance.
3. Determination of the relative values of the weights.
4. Transformation of the relative values into absolute values.

Operations 1 and 2 have been discussed in §§ 67 and 68, respectively. Operations 3 and 4 will now be considered.

92. Determination of the Relative Values of the Weights. — The 5 mg. weight from the analytical set is placed on the right-hand pan, a 5 mg. weight from the auxiliary set is placed on the left-hand pan, and the equilibrium point determined as previously described. The 5 mg. weight is now taken off the right-hand pan and the rider placed at division 5.0 on the beam and the new equilibrium point determined. The difference between these two equilibrium points divided by the sensibility for no load in the pans gives us the amount by which the rider is heavier or lighter than the 5 mg. weight. For the purposes of the present calibration, it is necessary to determine the difference between the two equilibrium points to the second decimal place, but in ordinary weighings it is sufficient to determine the difference to only one decimal place.

Suppose that the first equilibrium point was 9.85 and the second was 10.07, while the sensibility for no load was 2.7. We then have 0.22 divided by 2.7 which equals 0.08 unit, which is the amount by which the 5 mg. weight and the rider differ. Since the second equilibrium point was further to the right than the first, it is at once evident that the rider is lighter than the 5 mg. weight; hence, since we arbitrarily assigned a relative value of

5 *units* to the 5 mg. weight, the rider = 5.00 − 0.08 = 4.92 units. It is necessary to get the relative values to the hundredth of a unit, but not to the thousandth.

The next thing to do is to get the values of the 10 mg. weights in terms of the 5 mg. weight and the rider; the principle being that we always get the value of the next higher denomination in terms of those that precede it.   The 5 mg. weight from the analytical set is placed in the right-hand pan and the rider is placed at 5.0 on the balance beam; a 10 mg. weight from the auxiliary set is placed on the left-hand pan and the equilibrium point is determined.   The 10 mg. weight from the analytical set is now substituted in the right-hand pan for the 5 mg. weight and the rider, and the new equilibrium point is noted.   Whence, as before, we calculate how much heavier or lighter the 10 mg. weight is with reference to the sum of the 5 mg. weight plus the rider.   Suppose that the 10 mg. weight is 0.15 unit heavier, then we have: 10 mg. weight = 5.00 + 4.92 + 0.15 = 10.07 units.

Table 12

RELATIVE VALUES OF A SET OF WEIGHTS

Denomination	Relative Value	Denomination	Relative Value
5 mg.	5.00	1 g.	991.92
Rider	4.92	2′	1,984.16
10′ mg.	10.07	2″	1,984.08
10″	10.07	5	4,960.64
20	19.93	10′	9,920.95
50	49.70	10″	9,920.83
100′	99.25	20	19,842.35
100″	99.18	50	49,606.02
200	198.53		
500	496.27		

It is advisable to make each calculation at the time that the weighing is made, because such calculation serves as a check upon the accuracy of the work.   It is obvious that if the weights were correct among themselves, the relative values of the 10's would be twice those of the 5's, the 20's twice those of the 10's, etc.

Since, in a good set of weights, the divergence from this relationship is very slight, we have at hand a simple method by which we can judge whether the observed divergence is large enough to excite suspicion or not.

The value of the other 10 mg. weight in the analytical set is similarly determined. The value of the 20 mg. weight is then determined in terms of the two 10 mg. weights; the 50 mg. weight in terms of the 20, the two 10's, the 5 mg. weight and the rider; and so on for the whole set. At the end of this procedure we have a series of values similar to those given in Table 12.

93. *Transformation of Relative Values into Absolute Values.*— From the preceding relative values we can get the absolute values just as soon as we know the absolute value of one of the heavier weights in the set. The 10′ g. weight is usually selected for this purpose, and its value determined by comparison with a known standard weight by the method of substitution.[21] The absolute values of the other weights can then be evaluated by proportion or by the method of approximation to be described. Since proportion involves calculations with numbers having five to seven digits, the method of approximation is to be preferred since it employs simpler arithmetic.

Suppose that the absolute weight of the 10′ g. weight was found to be 10,000.20 mg. by comparison with a known standard; then it follows that 9920.95 units = 10,000.20 mg. or for the accuracy in hand, that 1 unit = 1.01 mg.

We now notice that the relative value of the 50 g. weight is 1.27 units heavier than five times the relative value of the 10′ g. weight; therefore, the absolute value of the 50 g. weight is 1.28 mg. heavier than five times the absolute value of the 10′ g. weight, or 50,001.00 mg. + 1.28 mg. = 50,002.28 mg.

In a similar manner, the relative value of the 20 g. weight is 0.45 units heavier than twice the relative value of the 10′ g. weight; therefore, the absolute value of the 20 g. weight is 0.45 mg. heavier than twice the absolute value of the 10′ g. weight, or 20,000.40 mg. + 0.45 mg. = 20,000.85 mg.

[21] Every laboratory should have a known standard weight in its possession. The National Bureau of Standards, Washington, tests and certifies the accuracy of standards submitted but it does not manufacture or sell such standards. For regulations governing tests, see their *Circular* No. 3, mentioned in § 60.

We proceed in this way to get the absolute value of all the other weights in the set, carrying our calculations to the hundredth of a milligram, and then rounding off our figures to the tenth of a milligram. Thus for the set of weights under consideration, we have the values given in Table 13.

Table 13

CALIBRATION OF WEIGHTS

Denomination	Relative Value	Absolute Value	"Rounded-off" Absolute Value
5 mg.	5.00 units	5.04 mg.	5.0 mg.
Rider	4.92	4.96	5.0
10′ mg.	10.07	10.15	10.2
10″	10.06	10.14	10.1
20	19.93	20.09	20.1
50	49.70	50.09	50.1
100′	99.25	100.06	100.1
100″	99.18	99.98	100.0
200	198.53	200.12	200.1
500	496.27	500.24	500.2
1 g.	991.92	999.84	999.8
2′	1,984.16	2,000.01	2,000.0
2″	1,984.08	1,999.93	1,999.9
5	4,960.64	5,000.26	5,000.3
10′	9,920.95	10,000.20	10,000.2
10″	9,920.83	10,000.08	10,000.1
20	19,842.35	20,000.85	20,000.9
50	49,606.02	50,002.28	50,002.3

A convenient method of procedure in obtaining the absolute values of a set of weights has been devised by Ellis H. Blade.[22] By way of illustration let us consider the calculation of the absolute values of a set of weights, the relative values of which are given in Table 14. The procedure employed may be summarized as follows:

[22] *Ind. Eng. Chem., Anal. Ed.* **11**, 499 (1939).

Table 14

CALIBRATION OF WEIGHTS: MODIFIED METHOD

1 Denomination	2 Relative Value, units	3 10 S Aliquots, units	4 Difference, units	5 Difference, mg.	6 10 S Aliquots, mg.	7 Absolute Value, mg.	8 Rounded mg.	9 Correction, mg.
5 mg. Rider	5.00	4.96	0.04	0.04	5.00	5.04	5.0	0
10'	4.92	4.96	−0.04	−0.04	5.00	4.96	5.0	0
10''	10.07	9.92	0.15	0.15	10.00	10.15	10.2	0.2
10''	10.06	9.92	0.14	0.14	10.00	10.14	10.1	0.1
20	19.93	19.84	0.09	0.09	20.00	20.09	20.1	0.1
50	49.70	49.60	0.10	0.10	50.00	50.10	50.1	0.1
100'	99.25	99.20	0.05	0.05	100.00	100.05	100.1	0.1
100''	99.18	99.20	−0.02	−0.02	100.00	99.98	100.0	0
200	198.53	198.41	0.12	0.12	199.99	200.11	200.1	0.1
500	496.27	496.02	0.25	0.25	499.98	500.23	500.2	0.2
1 g.	991.92	992.04	−0.12	−0.12	999.96	999.84	999.8	−0.2
2'	1984.16	1984.07	0.09	0.09	1999.92	2000.01	2000.0	0
2''	1984.08	1984.07	0.01	0.01	1999.92	1999.93	1999.9	−0.1
5	4960.64	4960.18	0.46	0.46	4999.80	5000.26	5000.3	0.3
10'	9920.95	9920.35	0.60	0.60	9999.60	10000.20	10000.2	0.2
10''	9920.83	9920.35	0.48	0.48	9999.60	10000.08	10000.1	0.1
20	19842.35	19840.70	1.65	1.66	19999.20	20000.86	20000.9	0.9
50	49606.02	49601.75	4.27	4.30	49998.00	50002.30	50002.3	2.3
(10 S)	9920.35	9920.35	****	****	9999.60	Absolute Value of Standard Weight		

1. The *relative values* of all the weights are determined in terms of the 5 mg. weight by Borda's method of substitution described above.

2. The *relative value* of the standard weight (10 S) is found. The relative values of all the weights are then tabulated (Column 2). In this case a 10 g. standard was used, but any certified weight of 10 g. or more may be used. In general a heavy standard is preferable to a light one.

3. In Table 14, the absolute value of the standard weight is given as 9999.60, and its relative value as 9920.35. These figures are the basis of the two aliquot columns, which are obtained by subdividing 9920.35 and 9999.60, respectively, into 1/2, 1/5, 1/10, 1/20, 1/50, etc. (Columns 3 and 6.)

4. The *differences in units* given in column 4 are found by horizontal subtraction of the items in column 3 from those in column 2, taking the sign into account.

5. The ratio of the two values of the standard weight, 9999.60/9920.35 is 1.008. This factor converts the *difference in units* to *difference in mg.* (Columns 4 and 5.)

6. Finally, the *absolute values* (Column 7) are found by horizontal addition of the *differences* (Column 5) to the *aliquots* (Column 6). These should be rounded off to the nearest tenth, and the corrections tabulated as in column 9. These corrections should be compiled in a cumulative table for ready reference as described in § 94.

94. Table of Corrections. — Since it is very seldom that a set of weights is free from corrections, and it entails considerable labor to add up the values of the weights each time a weighing is made, the following scheme should be employed in order to minimize the likelihood of error and to save time.

In making a weighing, *always use the least number of weights possible and always use a single-primed weight in preference to a double-primed weight.* This procedure then makes possible the use of a table which shows at a glance how much must be added or subtracted in any given case, according to the weight on the pan. Thus Table 15 shows the corrections to be applied in connection with the use of the set of weights the values of which are given in Table 13.

Table 15

TABLE OF CORRECTIONS

Milligrams to be Added to (+) or Subtracted from (−) Given Weight on Pan									
mg.	10	20	30	40	50	60	70	80	90
	+0.2	+0.1	+0.3	+0.4	+0.1	+0.3	+0.2	+0.4	+0.5
100	+0.1	+0.3	+0.2	+0.4	+0.5	+0.2	+0.4	+0.3	+0.5	+0.6
200	+0.1	+0.3	+0.2	+0.4	+0.5	+0.2	+0.4	+0.3	+0.5	+0.6
300	+0.2	+0.4	+0.3	+0.5	+0.6	+0.3	+0.5	+0.4	+0.6	+0.7
400	+0.2	+0.4	+0.3	+0.5	+0.6	+0.3	+0.5	+0.4	+0.6	+0.7
500	+0.2	+0.4	+0.3	+0.5	+0.6	+0.3	+0.5	+0.4	+0.6	+0.7
600	+0.3	+0.5	+0.4	+0.6	+0.7	+0.4	+0.6	+0.5	+0.7	+0.8
700	+0.3	+0.5	+0.4	+0.6	+0.7	+0.4	+0.6	+0.5	+0.7	+0.8
800	+0.4	+0.6	+0.5	+0.7	+0.8	+0.5	+0.7	+0.6	+0.8	+0.9
900	+0.4	+0.6	+0.5	+0.7	+0.8	+0.5	+0.7	+0.6	+0.8	+0.9
g.	1	2	3	4	5	6	7	8	9
	−0.2	zero	−0.2	−0.1	+0.3	+0.1	+0.3	+0.1	+0.2
10	+0.2	zero	+0.2	zero	+0.1	+0.5	+0.3	+0.5	+0.3	+0.4
20	+0.9	+0.7	+0.9	+0.7	+0.8	+1.2	+1.0	+1.2	+1.0	+1.1
30	+1.1	+0.9	+1.1	+0.9	+1.0	+1.4	+1.2	+1.4	+1.2	+1.3
40	+1.2	+1.0	+1.2	+1.0	+1.1	+1.5	+1.3	+1.5	+1.3	+1.4
50	+2.3	+2.1	+2.3	+2.1	+2.2	+2.6	+2.4	+2.6	+2.4	+2.5

95. Exercise No. 1.   Calibration of a Set of Weights. — Following the directions given in the preceding paragraphs prove the rider and determine the sensibility of the balance.   After this has been completed, determine the relative values of the analytical weights and calculate their absolute values.   Construct a table of corrections similar to Table 15.

96. Balances of Special Design. — Where the precision required is of a higher order than that obtainable with the usual type of analytical balance, or where an attempt is made to diminish the time required or to simplify the procedure used in weighing, balances differing in design from the type described in § 63 are often employed.   A few of the more important balances of special design will be discussed in the succeeding paragraphs.

97. *The Magnetically Damped Balance.* — As shown in Figure 27, the magnetically damped balance is equipped with an aluminum plate *A* supported from the stirrup *S*. The plate which is
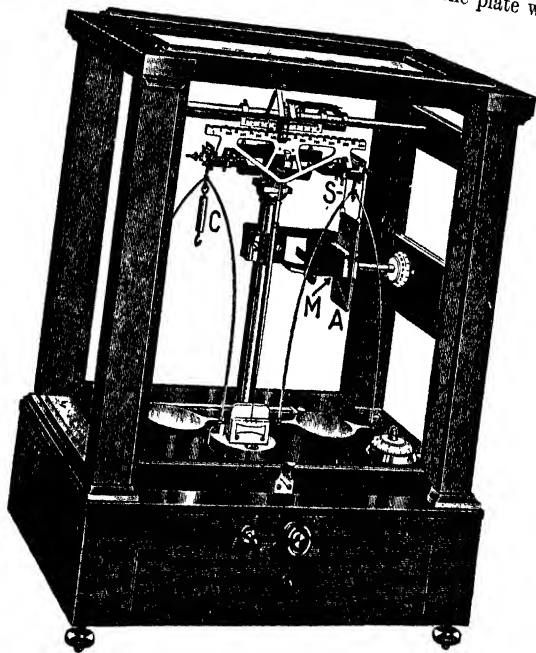

Fig. 27

Magnetically Damped Balance

counterpoised by *C* is suspended between the poles of the permanent magnet *M*. By this device the zero point can be quickly determined, for the motion of the Plate *A* in the magnetic field induces currents in the plate which sets up a magnetic field that opposes the motion of the plate and thereby brings the pointer directly to the zero point.

98. *The Air Damped Balance.* — The air damped balance uses air resistance against loosely fitting pistons in cylinders C and C', shown in Figure 28, to damp its swing and thereby arrive at the zero point quickly.

Fig. 28
Air Damped Balance
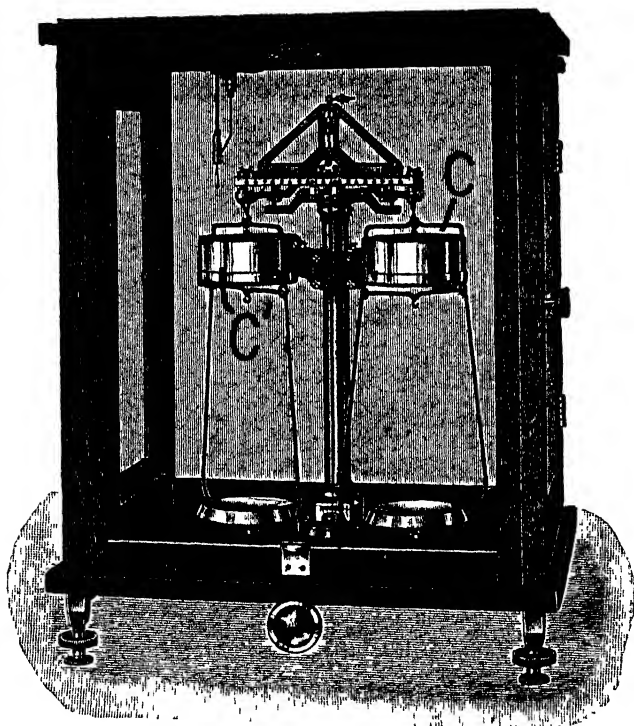
99. *The Chainomatic Balance.* — The chainomatic balance (Figure 29) is equipped with the Chain r, one end of which is attached to the right balance arm at c.   The other end is attached to the vernier v by means of the vernier hook, h.   By changing the amount of the chain supported by the beam, we can make the final adjustment in weighing.   We can thus weigh to a tenth

of a milligram without the necessity of using the smaller fractional weights or the rider.

b - Beam
c - Chain Carrier
e - Chain Eyelet
h - Vernier Hook
r - Chain
s - Graduated Column
v - Vernier

Relative position of Scale and Vernier on 18 mg. reading.

Same on 18.3 mg.
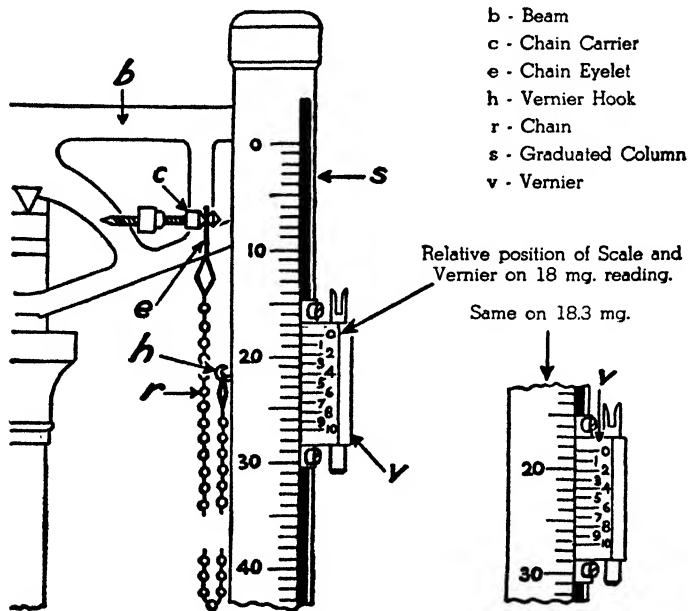
Fig. 29

View of Portion of Chainomatic Balance Showing Graduated Column and Vernier

100. *Microanalytical Balances.* — Balances used in microanalysis bear a close resemblance to the usual type of analytical balance described in § 63. However, the dimensions and weights of the parts, the material and workmanship are such as to yield a much higher sensibility than is obtainable with the usual type of balance. They are thus suitable for work requiring a high degree of precision.

101. Examples.

1. From the following data obtained in the calibration of a set of analytical weights by the method of substitution, determine the true values of the respective weights.

Denomination	Relative Values	Denomination	Relative Values
0.005 g.	0.00500	0.5 g.	0.49615
Rider	0.00508	1.0	0.99188
0.01′	0.00993	2.0′	1.98411
0.01″	0.00989	2.0″	1.98400
0.02	0.01990	5.0	4.96059
0.05	0.04968	10.0′	9.92079
0.1′	0.09921	10.0″	9.92086
0.1″	0.09913	20.0	19.84225
0.2	0.19845	50.0	49.60502

The value of the 10′ g. weight in comparison with the absolute value of a standard 10 g. weight by the same method was found to be 10.0002 g.

2. In weighing a brass object by the method of substitution and with the weights mentioned in § 93, the following weights were used: 20 g., 10′ g., 5 g., 0.5 g., 0.05 g. What was the weight of the object?

Ans.   35.5517 g.

3. Determine the ratio $R : L$ from the following data. When a 10 g. weight was placed in the right pan and a counterpoise weight in the left, 0.1 mg. had to be added to the left-hand pan. When the 10 g. weight was placed in the left-hand pan and the counterpoise weight in the right, 0.2 mg. had to be added to the left-hand pan. What was the weight of the counterpoise weight?   Ans. $\frac{R}{L} = 1.000015$.

4. The weight in air at a temperature of 20° of a Dumas bulb filled with benzene vapor is 24.9302 g., using brass weights. The weight of the bulb itself in air at 20° is 24.7238 g., and its capacity 143.01 ml. What is the true weight of the benzene vapor? The density of brass may be taken as 8.5, that of glass as 2.7, the weight of 1 ml. of air at 20° as 1.2 mg.

Ans.   0.3780 g.

5. A small cylinder of white metal weighed 58.1612 g. in air. When suspended by a platinum wire in water at 19° the weight was 50.4995 g. The wire suspended in water to the same depth weighed 0.3300 g. Brass weights of density 8.5 were used. What was the weight "in vacuo" and what was its volume?   Ans.   58.1626 g.   8.013 ml.

6. Using brass weights of density 8.0, and assuming that 1 ml. of air weighs 0.0012 g., calculate the difference between the weight in air of 1 g. of substance and the weight "in vacuo" when the density of the substance is 0.5, 1, 2, 4, 8 and 20. Plot the results with the densities as abscissæ and the differences as ordinates.

7. Using brass weights in air, a sample of aluminum and a sample of platinum were each found to weigh 40.0052 g. The density of the aluminum was 2.702 and that of the platinum was 21.40. Calculate the weight of each sample "in vacuo."

CHAPTER V

VOLUMETRIC MEASUREMENTS

102. General Considerations. — Because of the fact that so many methods of analysis are based upon the operation known as *titration,* the general problem of measuring the volumes of

A Burette
B. Measuring pipette
C. Volumetric pipette
D. Volumetric flask
E. Graduated Cylinder
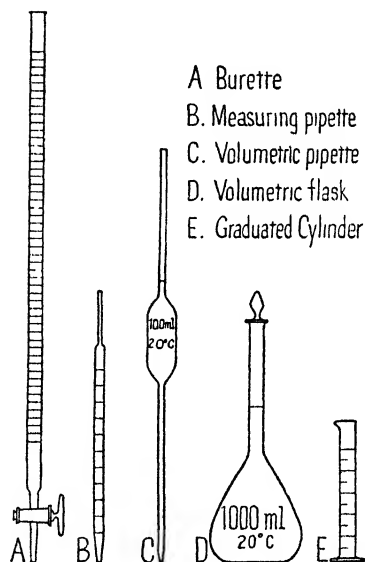
Fig. 30

Volumetric Glassware

solutions is one with which the analyst is concerned almost as frequently as he is with that of weighing. In carrying out such measurements, the use of certain graduated glass vessels of special design, particularly flasks, burettes, pipettes, and cylinders, plays an important part. Some pieces of volumetric glassware are shown in Figure 30. Before discussing these, however, it will be advantageous to present the theory which underlies *titration*

so that we may appreciate more fully the problem which confronts us in measuring the volumes of solutions.

In order to carry out the operation of titration, the constituent being determined must be in solution. We must also prepare a standard solution. This solution must contain a definite weight per unit volume of a reagent of such nature that, under given conditions, it will react with the constituent being determined. The operation of titration consists in adding the reagent to the solution of the constituent being determined until a chemically equivalent quantity of reagent has been added. Beyond this point the reagent can be observed to be in excess by means of some change in the solution, such as the appearance or disappearance of a color or of a precipitate, or an abrupt change in electrolytic conductance or oxidation potential. In many cases, an auxiliary reagent, known as an indicator, must be added in order to make the change apparent. Since the concentration of the standard solution is known and its volume is measured, the weight of the reagent used can be determined and the equivalent weight of the constituent sought can be ascertained.

From a consideration of the foregoing, it can be seen that, with respect to the use of a standard solution, the two following conditions must be satisfied:

1. Whatever unit of volume was originally used for the standard solution in determining its weight of reagent per unit volume, this same unit must always be employed in making subsequent titrations with the standard solution.

2. The weight of reagent contained in unit volume of a standard solution shall not vary, once it has been determined.

It is important therefore, in volumetric processes, first, that our several measuring vessels be graduated in terms of the same unit, and, second, that our measurements be made at one fixed constant temperature, because the value of a solution, that is the weight of a reagent per unit volume, changes with temperature.

103. Unit of Volume. — As far as the needs of any one laboratory are concerned, the various measuring vessels could be graduated in terms of any system of units consistent among themselves, but for the sake of general uniformity in the science, it is advisable to employ only the system that is founded on the

fundamental scientific unit of volume, the *liter*, as established by the International Commission of Weights and Measures. The Commission defines the liter as the volume occupied by the mass of one kilogram of pure water at its maximum density and under normal atmospheric pressure. The definition used by the United States Bureau of Standards [1] differs a little in its wording. It is: the liter is the volume occupied by a quantity of pure water at 4°C., having a mass of one kilogram. Substantially these definitions are equivalent.

The liter so defined is, according to recent determinations, a trifle different from the cubic decimeter,[2] being about 29 cubic millimeters larger. This difference amounts to about 0.029 part in 1,000. It follows that the one-thousandth part of a liter, which is also used as a unit of capacity and which is known as a milliliter, is in reality, a trifle larger than a cubic centimeter. The difference, 0.029 parts in 1,000, is insignificant in volumetric analysis, and the custom of using the term, *cubic centimeter*, to represent the one-thousandth part of a liter is often followed, although the term, *milliliter*, should, strictly speaking, be the term to use. The term milliliter is often abbreviated to ml.

104. Standard Temperature. — The capacity of a glass vessel is changed by changes in temperature. Consequently, in complying with the condition that the same unit of volume must apply to all our volumetric apparatus, attention must be paid to temperature, because if the vessels are used at temperatures different from that at which they were graduated, the graduations will represent different units of volume. It is necessary, therefore, not only that the several vessels be graduated in terms of the same unit, but also that the graduations refer to the same temperature. The temperature that has been adopted by the United States Bureau of Standards is 20°C. This temperature is known as the *Standard Temperature* and the Bureau will not recognize any other for volumetric apparatus. The reason for adopting this particular temperature is to be found in the fact

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[1] N. S. Osborne and B. H. Veazey, "The Testing of Glass Volumetric Apparatus," *Nat. Bur. Standards, Reprint No. 92*, p. 565, Washington (1908).

[2] Guillaume, "La Création du Bureau International des Poids et Mesures et son Œuvre," p. 258, Gauthier-Villars et Cie. Paris, 1927.

that it most nearly represents the average temperature of the laboratory, or at least a temperature that is readily attainable.

The foregoing remarks about temperature apply *a fortiori* in the carrying out of the further condition that the weight of reagent per unit volume of a standard solution shall not vary, once it has been determined. Obviously, if the standard solution is used at temperatures different from that at which it was standardized, the weight of reagent per unit volume will be different. This is easily apparent because the temperature change affects only the volume and not the mass of a solution. It therefore follows that standard solutions should be made up, have their values determined, and then be subsequently used all at the same temperature. Naturally, this temperature should be the same as that for which the volumetric apparatus is graduated, which, for our purposes, is the temperature of 20°.

105. Variation of Temperature. — While it is an easy matter to have all our apparatus graduated for 20°, and also an easy matter to make up our standard solutions and to standardize them for this same temperature, it is not always practicable, on account of the existing temperature of the laboratory, to use our apparatus at 20° or to bring the temperature of our standard solutions to 20°. It hence becomes of importance to determine the magnitude of the error which is introduced into volumetric procedure by using standard solutions at temperatures different from 20°. In doing this we will take it for granted that our apparatus is graduated for 20° and that our standard solutions have been standardized for this same temperature.

106. *Effect of Variation of Temperature on Capacity of Glass Volumetric Apparatus.* — With respect to the change in capacity of our glass volumetric apparatus with temperature, this is only slight, being approximately 1 part in 10,000 for 5° change in temperature. Thus, if we have a liter flask whose capacity is 1,000.0 ml. at 20°, its capacities at other temperatures would be:

Temperature	10°	15°	20°	25°	30°
Capacity in ml.	999.8	999.9	1000.0	1000.1	1000.3

It is to be noted, for glass apparatus, that the cubical capacity is a linear function of the temperature between 0° and 100°, so that,

knowing the change per degree and the capacity at any given temperature in this interval, we can calculate the capacity for any other temperature in the interval.

The glass measuring vessels commonly used in quantitative analysis change in capacity about 25 millionths of their capacity for a change of one degree centigrade. If we let C' and C represent the capacities of a glass container at the two temperatures t' and t, then it follows that

$$C' = C\,[1 + 0.000025\,(t' - t)].$$

If a flask has a capacity of 500.00 ml. at 20°, then its volume at 30° will be

$$C' = 500.00\,[1 + 0.000025\,(30 - 20)] = 500.12\ \text{ml}.$$

107. Effect of Variations of Temperature on Volumes of Solutions. — With respect to the change in the values of standard solutions, it is to be noted that the more concentrated the solution, the more the relative change. It is seldom that we work with standard solutions more concentrated than 0.2 M or less concentrated than 0.005 M, so that if we give the change for a 1.0 M solution, a 0.1 M solution, and water itself, we will have covered the extreme cases as well as the ordinary case. In this connection, it is to be remarked that the coefficient of expansion of solutions of different electrolytes is practically the same for similar concentrations; hence, the values given in Table 16 may serve as a general index of behavior:

Table 16

Effect of Changes in Temperature on Volumes of Solutions

Solution Employed	Volumes Occupied at Temperature Given				
(Composition at 20°)	15°	20°	25°	30°	35°
1.0 M HCl	996.7	1000.0	1001.3	1002.8	1004.7
0.1 M HCl	997.1	1000.0	1001.2	1002.6	1003.8
Water	999.1	1000.0	1001.1	1002.5	1004.2

The variation in volumes is from 1 to 3 parts per 1,000 per 5° change in temperature; the variation in the volumes in any given case also represents the variation in the value of the standard solution.

Putting the matter in somewhat different form, we may say that if we aim at a precision of 1 part per 1,000 in our work, our volumetric measurements must all be made within a compass of 2° including the standard temperature; if we extend this compass to 5° including the standard temperature, the precision will be only 2 parts per 1,000, and so on.

108. Other Factors Which Affect the Measurement of Volumes. — The other factors which we have to consider are the following four: cleanliness of apparatus, reading position of meniscus, method of filling and emptying, and design of apparatus.

109. Cleanliness. — We may enunciate it as an inviolable principle in volumetric analysis that every piece of volumetric apparatus, upon being used, shall answer the following test for cleanliness. *The test is to fill the container to capacity with distilled water and then to withdraw the water. If the container is clean, only an unbroken film will remain on its walls.* If it is dirty, the water will collect in drops which may introduce a large error in using the container. Usually the necessary cleaning can be effected by completely filling the vessel with *cleaning mixture* and allowing it to stand for several hours, then washing it with distilled water several times.

Cleaning mixture is a solution of potassium or sodium dichromate or of chromic acid in concentrated sulfuric acid. Potassium dichromate is not very soluble in concentrated sulfuric acid; consequently, it is not infrequent to find the chromate precipitated out from the cleaning mixture if potassium dichromate has been used. The solubility of potassium dichromate in 18 M sulfuric acid at room temperature is only about 5 g. per liter, whereas for $Na_2Cr_2O_7 \cdot 2H_2O$, it is 70 g. per liter. The greater solubility of sodium dichromate, as well as the fact that it is cheaper, makes its use preferable to that of potassium dichromate. In preparing cleaning solution 70 g. of $Na_2Cr_2O_7 \cdot 2H_2O$ should be dissolved in one liter of 18 M H_2SO_4 at room temperature. From time to

time thereafter, it is advisable to filter it through a little glass wool placed in the apex of a glass funnel; this procedure will remove any small particles or sludge which are often present and which are likely to stop up the tips of burettes in a most annoying manner.

If the treatment with cleaning solution fails to remove the contamination, the vessel should be filled with a 3 M solution of caustic soda, allowed to stand 20 to 30 minutes but no longer, rinsed with water and then treated with cleaning mixture as previously directed. Either an aqueous or an alcoholic solution of caustic soda may be used, but the latter is preferable. Alcohol often contains impurities extracted from the wooden barrel in which it is shipped for commerce; it is therefore advisable to distill the alcohol over potassium hydroxide beforehand. In no case should the use of hot water or the application of heat to volumetric apparatus be resorted to, because it may bring about a permanent enlargement in the capacity of the vessel, due to thermal "after effect."

After cleaning volumetric vessels, it is not generally necessary to dry them if they are to be used with standard solutions. The slight amount of water which remains after rinsing and draining is gotten rid of by rinsing the vessel two or three times with small amounts of the standard solution to be used, and allowing the vessel to drain thoroughly between rinsings. If it is necessary, however, to dry a vessel after cleaning as is the circumstance when flasks are to be calibrated, the vessel, after being rinsed with water, is further rinsed by means of alcohol and then dried by means of a gentle air blast.

110. Reading the Position of the Meniscus. — In measuring the volumes of liquids by means of volumetric apparatus, the lowest point of the meniscus is to be taken as the reading, except that in the case of dark-colored or opaque solutions where the bottom of the meniscus is not discernible, the plane of the upper periphery of the meniscus is to be taken as the reading. In observing the lowest point of the meniscus, it is very important that the line of vision be in the same horizontal plane as the bottom of the meniscus, otherwise the reading will be in error due to parallax; if the line of vision is downward, the meniscus will appear

higher than it really is, while if the line of vision is upward, the meniscus will appear lower, as illustrated in Figure 31.

By using apparatus on which all graduations extend at least halfway around, it is possible to avoid parallax by so placing the eye that, when observing the meniscus, the front and back portions of the graduation coincide. In certain lights of the day it is often a difficult matter, particularly with burettes, to recognize the lowest point of the meniscus unless the outline of the meniscus and the background are brought into contrast. This contrast can be produced by the simple device of holding in back of the meniscus a white background which has across it a black strip, and then so adjusting the background that the black field is either just below the bottom of
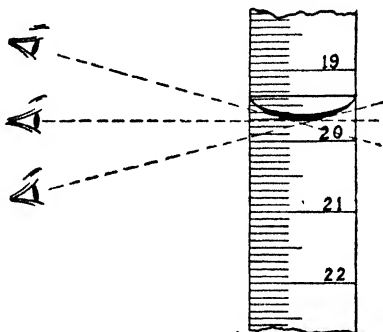

Fig. 31

Observation of Meniscus

the meniscus or extends a few millimeters above it, as may be necessary. A white card, about 12 cm. long by 8 cm. wide with a strip of black dull paper about 1.5 cm. wide pasted lengthwise across the middle portion of the card, answers admirably for the purpose.[3]

Floats. — The use of a float to give burette readings should never be countenanced because of the fact that if the float touches the wall of the burette, as it frequently does, it introduces an error into the reading.

111. Filling and Emptying of Volumetric Apparatus. — In using volumetric apparatus, it must always be borne in mind that its calibration has been effected by means of *water* in accordance with

[3] *Nat. Bureau of Standards, Reprint No. 92,* p. 567, referred to in § 103, recommends a different device which, however, is the same in principle. It is to clasp "around the graduated tube a collar-shaped piece of thick rubber tubing. When this collar is placed immediately below the meniscus and a white background employed, the profile of the meniscus is very definitely outlined and is practically coincident in position with the liquid surface, while if this precaution is neglected the apparent outline of the meniscus may be considerably in error."

a certain prescribed procedure, and, consequently, its use is predicated on the assumption that the solution to be measured shall not differ essentially from water with respect to its density, viscosity or surface tension because of the difference in the drainage effect brought about by these factors. Broadly speaking, aqueous solutions which are not more concentrated than one molar answer this requirement. If the solutions differ markedly from water, the same precision will not apply to their volumetric measurement as applies to water. In such cases, the chemist will have to determine the precision which applies and possibly will have to modify the procedure or the design of the apparatus.

Flasks. — In using flasks, it should always be observed that, after filling to the capacity mark, they should be well shaken so that the contents will be completely mixed.

When flasks are used to deliver, they should be emptied by gradually inclining them until, when the continuous stream has ceased, they are nearly vertical. After half a minute in this position, the mouth is brought in contact with the wet surface of the receiving vessel to remove the adhering drop.

Burettes. — In work with burettes it is preferable to use the zero mark each time. The burette should be filled nearly to the top and the setting to the zero mark made by slowly withdrawing the solution. In drawing the column down to zero, any air that may have been entrapped in the nozzle of the burette between the stop-cock and the tip will be forced out beforehand, thus removing a not infrequent source of error from the titration.

In withdrawing solutions from burettes, the latter should be held in a vertical position and, after the outflow has been finally stopped, the drop which adheres to the tip should be removed by touching it with the wet surface of the receiving vessel or through the intermediary of a stirring rod. Before taking the final reading of the meniscus, it is essential to wait 30 seconds in order that the effect of further drainage be negligible.

Burettes with rubber tips for use with alkaline solutions (Mohr's burette) are not recognized by the Bureau. When it is necessary to measure alkaline solutions as a matter of daily routine, the action of the alkali on the stop-cock of a glass-tipped burette may be obviated by using a silver stop-cock.

Pipettes. — In using pipettes which are calibrated to deliver one definite volume (transfer pipettes), the excess liquid adhering to the tip should be removed when the filling is completed. In emptying, they should be held in a vertical position, and after the continuous unrestricted flow ceases, the tip should be touched with the wet surface of the receiving vessel.[4] The portion of liquid then remaining in the constriction of the tip is left there; it should never be blown out.

In using pipettes which are graduated (measuring pipettes), the excess liquid adhering to the tip should be removed when the filling is completed. As regards other details of manipulation, the remarks made above with respect to burettes apply here.

Cylinders. — Graduated cylinders accepted by the Bureau for test must be marked *to contain* and are tested accordingly. When used *to deliver*, cylinders should be used as when used *to contain*, and should be emptied by gradually tilting them until, when the continuous stream has ceased, they are almost vertical. After draining in this position for half a minute, the drop should be removed by bringing the mouth of the cylinder lightly into contact with the wetted surface of the receiving vessel. Cylinders correctly graduated *to contain* within the allowed limits of error, are, in general, correct *to deliver* within twice these limits when the delivery is made in the above manner.

112. Design of Volumetric Apparatus. — As a result of an extended investigation of the various factors which enter into the measurement of volumes of liquids, the Bureau of Standards[5] has laid down certain specifications which apparatus must satisfy before it will be accepted by them for calibration. An abridgment of these specifications is given herewith; for further detail the reader must consult the original source.

General Specifications. — The material should be of the best quality of transparent glass, free from striæ, adequately resistant to chemical action, and possessing small thermal hysteresis.

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[4] This is in accordance with the recommendations of the International Committee on Analyses, Rome (1906), as adopted by the National Bureau of Standards and given in *Reprint No. 92*, p. 581 and referred to in § 103.

[5] *Ibid.*

The cross section of all apparatus must be circular and the shape must permit of complete emptying and drainage.

Instruments having a base or foot must stand solidly on a level surface, and the base must be of such size that the instruments will stand on a plane inclined at 15°.

Stoppers and stop-cocks must be so ground as to work easily and to prevent leakage.

The parts on which graduations are placed must be cylindrical for at least 1 cm. on each side of every mark, but elsewhere may be enlarged to secure the desired capacities in convenient lengths.

The graduations should be of uniform width, continuous and finely but distinctly etched, and must be perpendicular to the axis of the apparatus. All graduations must extend at least halfway around, and, on subdivided apparatus, every tenth mark, and, on undivided apparatus, all marks must extend completely around the circumference.

The space between two adjacent marks must not be less than 1 mm. The spacing of marks on completely subdivided apparatus must show no evident irregularities, and sufficient divisions must be numbered to indicate readily the intended capacity of any interval. Apparatus which is manifestly fragile or otherwise defective in construction will not be accepted.

Inscriptions.—Every instrument must bear in permanent legible characters the capacity in liters or milliliters, the temperature in Centigrade degrees at which it is to be used, the method of use, *i.e.*, whether to contain or to deliver, and, on instruments which deliver through an outflow nozzle, the time required to empty the total nominal capacity with unrestricted outflow must be likewise indicated.

Every instrument should bear the name or trademark of the maker. Every instrument must bear a permanent identification number, and detachable parts, such as stoppers, stop-cocks, etc., belonging thereto must bear the same number.

Special Requirements. — (a) Flasks. At the capacity mark or marks on a flask, the inside diameter should be within the following limits, and the neck of the flask must not be contracted above the graduation mark:

Capacity of flask (in ml.)

up to and including	2,000	1,000	500	250	200	100	50	25
Maximum diameter (in mm.)	25	20	18	15	13	12	10	8
Minimum diameter (in mm.)	18	14	12	10	9	8	6	6

The capacity mark on any flask must not be nearer the end of the cylindrical portion of the neck than specified below:

Capacity	*100 ml. or less*	*More than 100 ml.*
Distance from upper end	3 cm.	6 cm.
Distance from lower end	1 "	2 "

Flasks of 1 liter or more (but not less) may be graduated both to contain and to deliver, provided the intention of the different marks is clearly indicated.

(b) Burettes.   Only burettes emptying through a nozzle permanently attached at the bottom are accepted for test by the Bureau. The tip of the burette should be made with a gradual taper from 2 cm. to 3 cm., the taper at the extreme end being slight.   The Bureau recommends that the tip should be bent slightly and gives drawings showing approved forms of tips.   In the experience of the writers the use of bent tips is not as satisfactory as the use of straight tips.   A sudden contraction at the orifice is not permitted and the tip must be well finished.

The distance between the extreme graduations on the burette must not exceed 65 cm.   The rate of outflow of burettes must be restricted by the size of the tip and, for any graduated interval, the time of free outflow when tested with water at 20°, must not be more than three minutes nor less than the following for the respective lengths:

Length Graduated	Time of Outflow	Length Graduated	Time of Outflow
65 cm.	· 140 secs.	35 cm.	60 secs.
60 "	120 "	30 "	50 "
55 "	105 "	25 "	40 "
50 "	90 "	20 "	35 "
45 "	80 "	15 "	30 "
40 "	70 "		

(c) Transfer Pipettes.   Pipettes for delivering a single volume are designated "transfer pipettes" by the Bureau.

The suction tube of each transfer pipette must be at least 16 cm. long, and the delivery tube must not be less than 3 cm. nor more than 25 cm. long.

The inside diameter of any transfer pipette at the capacity mark must not be less than 2 mm. and must not exceed the following limits:

Capacity of pipettes (in ml.) up to and including	25	50	200
Diameter (in mm.)	4	5	6

The outside diameter of the suction and delivery tubes of transfer pipettes, exclusive of the tip, must not be less than 5 mm. The capacity mark on transfer pipettes must not be more than 6 cm. from the bulb.   Pipette tips should be made with a gradual taper from 2 cm. to 3 cm., the taper at the extreme end being slight.   A sudden contraction at the orifice is not permitted and the tip must be well finished.

The outlet of any transfer pipette must be of such size that the free outflow shall last not more than one minute and not less than the following for the respective sizes:

Capacity (in ml.) up to and including	5	10	50	100	200
Outflow time (in secs.)	15	20	30	40	50

(d) Measuring Pipettes.   The tip of the pipette should be made with a gradual taper from 2 cm. to 3 cm., the taper at the extreme end being slight.   A slight contraction at the orifice is not permitted and the tip must be well finished.

The upper end of any measuring pipette must not be less than 10 cm. from the uppermost mark, and the lower end not less than 4 cm. from the lowest mark.   The distance between the extreme graduations on a measuring pipette must not exceed 35 cm.   The rate of outflow of measuring pipettes must be restricted by the size of the tip and, for any graduated interval, the time of free outflow must not be more than three minutes nor less than the following for the respective lengths:

Length graduated (cm.)	35	30	25	20	15
Outflow time (secs.)	60	50	40	35	30

☞ (e) Cylinders. Only cylinders graduated *to contain* will be accepted for test by the Bureau. The inside diameter of cylinders must not be more than one-fifth the graduated length.

Delivery Time. — The delivery time marked on any instrument must be within the limits prescribed in the specifications and the error permitted in the marked delivery time is as follows:

Delivery Time Less Than and Including	Limit of Error
15 secs.	3 secs.
20 "	4 "
30 "	6 "
50 "	8 "
100 "	15 "
200 "	20 "

113. Precision In Volumetric Measurement. — The precision which is attainable in volumetric measurements when apparatus of standard design is used and the prescribed procedure already outlined with respect to the observance of temperature, reading the position of the meniscus, and method of filling and emptying is followed, is subjoined herewith in Table 17. From an examination of the figures it will be seen that, if we aim at a precision of 1 part per 1,000 in our measurements, then we must employ volumes not less than 25 ml. Further, the error of the indicated capacity of any ten consecutive subdivisions must not exceed one fourth the capacity of the smallest subdivision.

Table 17

LIMITS OF ERROR AND CAPACITIES OF VOLUMETRIC APPARATUS

Capacity Less Than and Including	FLASKS Limit of Error	
	If to Contain	If to Deliver
25 ml.	0.03 ml.	0.05 ml.
50 "	.05 "	.10 "
100 "	.08 "	.15 "
200 "	.10	.20 "
300 "	.12 "	.25 "
500 "	.15 "	.30 "
1,000 "	.30 "	.50 "
2,000 "	.50 "	1.00 "

Table 17 (cont.)

BURETTES AND MEASURING PIPETTES

Capacity of Total Graduated Portion Less Than and Including	Limit of Error of Total or Partial Capacity	
	Burettes	Measuring Pipettes
2 ml.	....	0.01 ml.
5 "	0.01 ml.	.02 "
10 "	.02 "	.03 "
30 "	.03 "	.05 "
50 "	.05 "	.08 "
100 "	.10 "	.15 "

TRANSFER PIPETTES

Capacity Less Than and Including	Limit of Error
2 ml.	0.006 ml.
5 "	.01 "
10 "	.02 "
30 "	.03 "
50 "	.05 "
100 "	.08 "

CYLINDERS

Capacity of Total Graduated Portion Less Than and Including	Limit of Error of Total or Partial Capacity	When the Smallest Subdivisions Are Not More Than	Limit of Error of Any Ten Consecutive Divisions
30 ml.	0.06 ml.	0.2 ml.	0.1 ml.
50 "	.10 "	1.0 "	.2 "
100 "	.30 "	2.0 "	.4 "
200 "	.50 "	10.0 "	1.0 "
500 "	1.20 "	20.0 "	2.0 "
1,000 "	2.00 "		
2,000 "	4.00 "		

114. Calibration of Apparatus.[6] — While volumetric apparatus of a precision equal to that called for by the specifications of the Bureau of Standards can now be obtained, much of the apparatus on the market does not come up to these requirements, consequently it cannot be too strongly insisted upon that no piece of apparatus should be used unless it has first been calibrated either by one of the bureaus or by the analyst himself.

The difficulty in regard to calibration arises, not from the concept involved with respect to the liter, which we have only to picture as an invariable region of space, but rather from the practical question of how much water at any given temperature must be weighed out in air when brass weights are used, in order that the volume of water may be such that the glass container, calibrated by means of this water, will contain exactly one liter or the necessary number of milliliters at 20°.

115. *Calibration of Flasks.* — Let us suppose that it is required to calibrate a flask to contain 500 ml. at 20°. Let us also suppose that the calibration is to be performed at 15°. If the flask is to have a capacity of 500.00 ml. at 20°, then its capacity at 15° can be determined from

$$C' = C [1 + 0.000025 (t' - t)]$$

where C' and C are the capacities at temperatures t' and t. Substituting,

$$C' = 500.00 [1 + 0.000025 (15 - 20)] = 499.94 \text{ ml.}$$

This is the capacity the flask must have at 15° if it is to contain 500 ml. at 20°. The "in vacuo" weight, W_v, of water which this flask will contain at 15° can be determined by using Table 8 (Chapter IV) and the relationship

$$W_v = D C'$$

where D is the density of water at the temperature at which the calibration is performed. Substituting in the above equation,

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[6] For methods of calibration where the capacities of the vessels are determined by comparing them with the capacities of standard pipettes, which are so graduated as to allow a direct reading of the volumes, see Olsen, "Quantitative Chemical Analysis," referred to in § 11; also Morse and Blalock, *J. Am. Chem. Soc.*, **16**, 479 (1894).

we have
$$W_v = 0.99913 \times 499.94 = 499.51 \text{ g.}$$

Since the weighing must be made in air, we must calculate the weight, in air, of the water which, in a vacuum, weighs 499.51 g. This can be done by means of the relationship (§ 81)

$$W_a = W_v \frac{1 - \dfrac{S}{D}}{1 - \dfrac{S}{D'}}.$$

Substituting 0.00120 for S, the density of air at 15°, 8.40 for D', the density of brass, and 0.99913 for D, the density of water at 15° we get

$$W_a = 499.51 \frac{1 - \dfrac{0.00120}{0.99913}}{1 - \dfrac{0.00120}{8.40}} = 498.98 \text{ g.}$$

If a glass container is calibrated at 15° with this weight of water, weighed in air at 15°, it will contain 500.00 ml. at 20°.

In the above calculations we have multiplied C' by D and then multiplied the product by

$$\frac{1 - \dfrac{S}{D}}{1 - \dfrac{S}{D'}}$$

or

$$W_a = C'D \frac{1 - \dfrac{S}{D}}{1 - \dfrac{S}{D'}} = C[1 + 0.000025\,(t' - t)]\,D\,\frac{1 - \dfrac{S}{D}}{1 - \dfrac{S}{D'}}$$

whence

$$W_a = C[1 + 0.000025\,(t' - t)]\,\frac{D - S}{1 - \dfrac{S}{D'}}.$$

By means of this relationship we can calculate the number of grams of water which must be weighed in air with brass weights at any temperature t', in order that the glass container, calibrated by means of this water, shall have a capacity of one liter at 20°.

The results of such calculations are given under G in Column 2 of Table 18. The corresponding weights, g, for one milliliter are

Table 18

WEIGHTS IN AIR OF WATER AT TEMPERATURES t' REQUIRED TO CALIBRATE
GLASS APPARATUS FOR 20° AND VOLUMES V OF GLASS CONTAINERS AT 20°
WHICH AT TEMPERATURES t' CONTAIN ONE GRAM OF WATER WEIGHED
IN AIR AT TEMPERATURE t'

1	2	3	4	1	2	3	4
t' (°C)	G (Grams)	g (Grams)	V (Milliliters)	t' (°C)	G (Grams)	g (Grams)	V (Milliliters)
15	997.96	0.99796	1.0020	26	995.91	0.99591	1.0041
16	997.82	0.99782	1.0022	27	995.66	0.99566	1.0044
17	997.67	0.99767	1.0023	28	995.41	0.99541	1.0046
18	997.52	0.99752	1.0025	29	995.14	0.99514	1.0049
19	997.35	0.99735	1.0027	30	994.87	0.99487	1.0052
20	997.18	0.99718	1.0028	31	994.55	0.99455	1.0055
21	996.99	0.99699	1.0030	32	994.23	0.99423	1.0058
22	996.80	0.99680	1.0032	33	993.91	0.99391	1.0061
23	996.58	0.99658	1.0034	34	993.60	0.99360	1.0064
24	996.37	0.99637	1.0036	35	993.27	0.99327	1.0068
25	996.14	0.99614	1.0039				

given in Column 3. Column 4 gives the volume V of a glass container at 20° which at temperature t' contains one gram of water weighed in air at temperature t'.

The following details of manipulation may be employed in the calibration of the flask under consideration. We place the clean, dry flask and brass weights, corresponding to its capacity at 20°, on the right-hand pan of a large laboratory balance capable of weighing to 0.01 g. In the case under consideration, we would use a 500 ml. flask and weights totaling 500.00 g. We then counterpoise with lead shot, or some other convenient material, and observe the equilibrium point of the balance. We next remove from the right-hand pan 0.99796 × 500.00 or 498.98 g. after which we add distilled, air-free water to the flask until the same equilibrium point is restored, being careful that no

drops of water adhere to the neck of the flask.   We then carefully mark the level of the water meniscus by means of a label.   If we wish to mark the flask permanently, a line can be made at the determined position by etching with hydrogen fluoride.   This flask will have a capacity of 500 ml. at 20°.

It may be required to determine the capacity of a flask which has previously been marked.   Let us suppose that we wish to determine the capacity at 20° of a liter flask.   Also let us suppose that this determination of capacity is carried out at 30°. The flask and 1,000.00 g. are placed on the right-hand pan and counterpoised with shot.   On consulting Table 18, we remove 994.87 g. from the right-hand pan; the flask is then filled to the mark with water.   Let us suppose the load on the right-hand pan is too small to produce equilibrium and 0.50 g. must be placed on this pan to restore equilibrium.   The weight of water added was $994.87 - 0.50 = 994.37$ g.   If we let C represent the capacity of the flask at 20°, we have

$$C = \frac{994.37}{994.87} \times 1,000 = 999.50 \text{ ml}$$

The same result can be obtained as follows:

$$C = 1,000.00 - 0.50 = 999.50 \text{ ml.}$$

where 0.50 ml. is the capacity of a glass container at 20°, which, at 30°, contains 0.50 g. of water when weighed in air at 30°. This volume is obtained with aid of Column 4 of Table 18.

Suppose that on adding water to the mark, 0.70 g. must be removed from the right-hand pan to restore equilibrium, then the weight of water added is $994.87 + 0.70 = 995.57$ g. and the capacity C of the flask at 20° can be determined by

$$C = \frac{995.57}{994.87} \times 1,000 = 1,000.70 \text{ ml.}$$

A glass vessel which contains at 30° 0.7000g. of water, weighed in air with brass weights at 30°, will have a capacity at 20° of 0.7036 ml.   Hence, the capacity of the flask can be determined by an alternative method as follows:

$$C = 1,000.00 + 0.70 = 1,000.70 \text{ ml.}$$

116. *Calibration of Burette.* — The burette to be calibrated should be thoroughly cleaned with cleaning solution and should have its stop-cock lubricated so that it turns easily. Care should be taken to avoid clogging the tip of the burette with lubricant. The burette is then filled with water. It is important to make sure that no air bubbles remain in the burette. If any are observed, water must be run from the burette until they are removed. Sufficient water is then added to bring the level above the zero mark, after which water is run from the burette in a series of drops until the meniscus coincides with the zero mark. If a drop of water adheres to the tip it is removed with a stirring rod. A weighing bottle, or a small flask which has previously been weighed, is placed beneath the burette and water is run into the container until the level in the burette is near the 5.00 ml. mark. Thirty seconds are allowed to elapse before taking the final reading of the burette. If a drop adheres to the tip it is added to the contents of the container by bringing the wall of the container in contact with the drop. The container and the water are then weighed to the nearest 5 mg. Proceeding at intervals of about 5 ml., the same procedure is continued until the meniscus coincides exactly with the 50.00 ml. mark. The weights and volumes observed are tabulated as shown in the first, second, and third columns of Table 19.

Table 19

CALIBRATION OF BURETTE No. 68

Burette Reading	Apparent Volume	Weights	True Volume	Error	Total Volume	Total Correction
0.00						
5.02	5.02	5.01	5.02	0.00	5.02	0.00
10.10	5.08	5.08	5.09	+0.01	10.11	+0.01
15.05	4.95	4.91	4.92	−0.03	15.03	−0.02
20.00	4.95	4.94	4.95	0.00	19.98	−0.02
25.20	5.20	5.21	5.22	+0.02	25.20	0.00
30.13	4.93	4.90	4.91	−0.02	30.11	−0.02
35.15	5.02	5.02	5.03	+0.01	35.14	−0.01
40.06	4.91	4.94	4.95	+0.04	40.09	+0.03
45.24	5.18	5.21	5.22	+0.04	45.31	+0.07
50.00	4.76	4.69	4.70	−0.06	50.01	+0.01

Suppose the calibration is performed at 15°.   Table 18 gives the weight in air at 15° of the water delivered by a glass container at 15° which, at 20°, would deliver exactly 1.00 ml., namely 0.99796 g.   By dividing this value into the weight in air at 15° of the water delivered by the burette between successive readings, we get the volume delivered by the burette at 20°.   This same procedure is followed for each quantity of water withdrawn from the burette.   The results are given in the fourth column of Table 19. The differences between the values in this column and the corresponding values in the second column give the corrections for each interval of 5 ml.   The last column gives the total correction to be applied when a titration is started at the zero mark and stopped at the corresponding total volume.   In the calibration of the burette the data should be tabulated as illustrated in the above example.

117. Calibration of Pipettes. — The pipette to be calibrated is filled above the mark with water.   The water is allowed to run out in a series of drops until the meniscus coincides with the mark.   If a drop adheres to the tip it is removed.   Then the water in the pipette is delivered to a small flask or weighing bottle.   If a drop adheres to the tip it is removed by touching it to the wall of the container.   If a drop still remains inside the tip it is permitted to remain there.   The weight of the water is then determined.   The calculation of the volume delivered is exactly the same in principle as that employed in the calibration of a burette, described in the preceding paragraph.

118. Exercise No. 2. Calibration of Volumetric Apparatus. — Following the procedures described in the foregoing paragraphs, calibrate any of the pieces of apparatus listed below which may require calibration for the work in hand.

(a) Flask
(b) Burette
(c) Pipette

119. Examples.

1. What is the weight of a liter of water when weighed in air at a temperature of 25° and 760 mm. pressure, using brass weights?

Ans.   996.04 g.

2. What error is introduced by using at 30° a solution of 0.1 M HCl that has been standardized at 20°?   Ans.   2.6 parts per 1,000.

3. In determining the capacity of a liter flask for 20°, how accurately must the temperature of the water be measured in order that the calibration be accurate to 0.1 ml.?　　　　　.　　　　　Ans.　±0.5°.

4. It is required to make up one liter of an exactly tenth molar solution of hydrochloric acid. After diluting the roughly calculated volume of 12 *M* HCl to one liter, it was found upon titration that 40.00 ml. of the solution contained 0.2592 g. of HCl. The calculated volume of this solution was measured out, using for the purpose a 500 ml. graduated flask and a 50 ml. burette. This volume was diluted to the mark in a 1,000 ml. graduated flask. Assuming that the burette can be read to 0.02 ml., and the graduated flasks to 0.2 ml., and assuming no other errors, what is the total amount by which this solution may differ from 0.1 *M*?
Ans.　0.7 part per 1,000.

5. A flask has a capacity of 1000.00 ml. at 20°. Its volume coefficient of expansion is 0.000025. Calculate its capacity at 35°.

6. What capacity will a flask have at 16° if its capacity at 20° is 1000.00 ml. (volume coefficient of expansion = 0.000025)?

7. Calculate the weight of water, weighed in air at 16° with brass weights, which will fill the flask of problem 6 at 16°.

8. 199.20 g. of water weighed in air with brass weights at 25° was used in calibrating a flask at 25°. Calculate the capacity of the flask at 20° (volume coefficient of expansion of glass = 0.000026)?

9. Let us suppose that at 30° we wish to calibrate for 20° a 200 ml. flask which had previously been marked. The flask and 200 g. are placed on the right-hand pan of the balance and counterpoised with shot. The appropriate weight is then removed from the right-hand pan and the flask is filled to the mark with water. In order to establish equilibrium 0.30 g. is added to the right-hand pan. Calculate the capacity of the flask at 20°.

10. In the calibration of a burette at 24° the following burette readings and corresponding weights in air with brass weights of the flask and contents were obtained. Calculate the error involved at each reading and the correction to be applied at 20°.

Burette reading (ml.) ...	0.00	10.11	20.02	30.12	40.00	50.00
Weights (g.)	30.52	40.62	50.47	60.58	70.55	80.45

PROPERTIES OF AQUEOUS SOLUTIONS OF ELECTROLYTES

120. Conductance and Ionization. — There is much evidence to indicate that substances and solutions which conduct an electric current and undergo electrolysis contain positively and negatively charged ions. Substances which contain ions, or which produce ions when dissolved in a solvent, are known as *electrolytes*. A substance or a solution of a substance which will not conduct a current and which cannot be electrolyzed is supposed not to contain ions and is known as a *non-electrolyte*.

Water solutions of electrolytes are so frequently encountered in quantitative analysis that it is desirable, at this point, to consider briefly some of their properties.

121. Strong Electrolytes. — There is considerable evidence to indicate that electrolytes differ widely in the extent of their ionization. Some electrolytes appear to be completely ionized. NaCl in the solid or liquid states, or as a solute in water, illustrates this class of electrolyte. This conclusion appears warranted when we consider the work of W. H. Bragg and W. L. Bragg [1] and of Debye [2] and others. It appears that Na and Cl are not combined to form molecules in solid NaCl but are separated and spaced in a definite pattern or crystal lattice, probably as Na ions and Cl ions. When we consider that water, due to its high dielectric property, diminishes the attractive forces between adjacent positive and negative charges to about 0.0124 times what they are in pure NaCl, it appears quite unlikely that many molecules of NaCl exist in water solution. When additional water is added to a moderately concentrated solution containing an equivalent weight of NaCl, a small increase takes place in the electrical conductance of the NaCl. The distances between the

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[1] W. H. Bragg and W. L. Bragg, reference given in § 11.

[2] Debye and Hückel, *Physik. Z.*, **24,** 185, 305 (1923); Debye, *Trans. Faraday Soc.*, **23,** 334 (1927); Hückel, *Ergeb. exakt. Naturw.*, **3,** 199, 276 (1924).

ions in the solution have been increased as a result of dilution. From theoretical considerations developed by Debye and Hückel, it can be shown that when these distances are increased, the conductance of one equivalent of the solution should increase. This follows from the consideration that the forces existing between electrically charged ions diminish as the distances between ions are increased, and also from the further consideration that the smaller these interionic forces, the more easily can the ions migrate through the solution.   Quantitative measurements show that the increase in the equivalent conductance of NaCl with dilution is practically all accounted for by the increase in the distances between ions.   It is unnecessary, therefore, to account for this increase in equivalent conductance by supposing that there is an increase in the number of ions in the solution.   We therefore need not conclude that dilution of the solution has resulted in increasing the extent of ionization of NaCl.   It appears reasonable to conclude that the NaCl is completely ionized.

Furthermore, when NaCl is dissolved in water, it depresses the freezing point of the solution almost twice as much as does an equal concentration of non-electrolyte.   If the NaCl is completely ionized, its concentration of solute particles will be exactly twice that of the solution of non-electrolyte.   The fact that the depression produced by the NaCl falls a little short of being exactly twice that produced by the non-electrolyte can be practically completely accounted for if we take into consideration the interionic forces between the ions of the NaCl.   It is not necessary, therefore, to suppose that the NaCl is less than 100% ionized.

On the basis of these considerations, we shall regard NaCl, at least in solutions of moderate concentration, as being completely ionized.   Experiments and calculations similar to those involving NaCl have been performed with other salts with similar results so that we can consider, for all practical purposes at least, that many salts are completely ionized in water solutions of moderate concentration.

There is considerable evidence to show that many electrolytes, while probably not completely ionized in water solution, exist to a very large extent in the form of ions.   HCl is an illustration of this class of electrolyte.   Pure liquid HCl has a very low con-

ductance, indicating a small extent of ionization, whereas a dilute water solution conducts well enough to indicate practically complete ionization. It seems probable, on the basis of the results of many experiments,[3] to consider that when HCl is dissolved in water the following reaction occurs:

$$HCl + H_2O \rightleftarrows OH_3^+ + Cl^-.$$
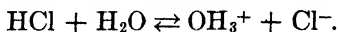
Other substances, such as HBr, HNO_3 and H_2SO_4, probably yield ions in solution in a similar manner. The oxonium ion, OH_3^+, formed by the interaction of an acid and H_2O, is responsible for some properties of the solution commonly referred to as acid properties. However, for the sake of simplicity in succeeding discussions, this ion will be represented by the simple hydrogen ion H^+, and the above equation will be written,

$$HCl \rightleftarrows H^+ + Cl^-.$$
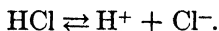
Electrolytes which are completely ionized or in which the extent of ionization is nearly complete are known as strong electrolytes. This group of substances includes most salts, a few acids, among which are HCl, HI, HBr, H_2SO_4, and HNO_3, and a few bases, among which are NaOH, KOH, and $Ca(OH)_2$. In calculations we shall consider strong electrolytes as being completely ionized, unless otherwise specified. A 0.01 M solution of HCl would be 0.01 M with respect to both H^+ and Cl^- and a 0.1 M solution of $BaCl_2$ would be 0.1 M with respect to Ba^{++} and 0.2 M with respect to Cl^-.

122. Weak Electrolytes. — There is considerable evidence to show that many electrolytes are only slightly ionized in solutions, of ordinary concentrations. Acetic acid, CH_3CO_2H, illustrates this class of electrolyte. The increase of the equivalent conductance of CH_3CO_2H on dilution cannot all be accounted for on the basis of an increase in the distances between the electrically charged ions. Most of this increase in equivalent conductance must be accounted for in some other way, and consequently it appears reasonable to suppose that addition of water has resulted

[3] Brönsted, *Chem. Rev.*, **5**, 231 (1928); Hall, *J. Chem. Education*, **7**, 782 (1930); *Chem. Rev.*, **8**, 191 (1931); Bjerrum, *Chem. Rev.*, **16**, 287 (1935).

in an increase in the number of ions in the solution, and therefore in an increase in the per cent of ionization of the acetic acid.

Furthermore, solutions of acetic acid in ordinary concentrations fall far short of producing a depression of the freezing point twice as great as that produced by an equal concentration of non-electrolyte. The smallness of this depression cannot be accounted for on the basis of the effect of inter-ionic forces. It is reasonable to suppose, therefore, that the acetic acid is much less than 100% ionized. The addition of water probably results in the formation of oxonium ion and acetate ion according to the equation,

$$CH_3CO_2H + H_2O \rightleftharpoons OH_3^+ + CH_3CO_2^-.$$
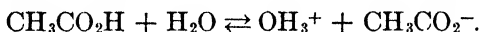
Omitting the molecule of water involved we shall express this change as follows:

$$CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-.$$
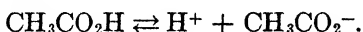
Similar experiments and calculations on many acids and bases and a few salts, have led to similar results. Among the salts which give these results are the mercuric, stannic and cadmium halides and lead acetate. Substances, the extent of ionization of which is relatively small, are known as weak electrolytes.

123. Calculation of Ion Concentrations in a Solution of a Weak Electrolyte from the Fraction Ionized. — To illustrate the calculation of ion concentrations in solutions of weak electrolytes, let us consider the case of acetic acid. In 0.100 M solution, at 25°, acetic acid has an equivalent conductance, Λ_c, of 5.200 reciprocal ohms. The sum of the equivalent conductances of hydrogen ion and acetate ion, namely the equivalent conductance of acetic acid at infinite dilution, Λ_o, is 385.3 reciprocal ohms[4] at 25°. The fraction, α, of the acetic acid ionized in 0.100 M solution is obtained from,

$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{5.200}{385.3} = 0.0135.$$

It follows that in this solution,

$$[H^+] = [CH_3CO_2^-] = 0.100 \times 0.0135 = 1.35 \times 10^{-3},$$

and that

$$[CH_3CO_2H] = 0.100 \times 0.9865 = 9.86 \times 10^{-2}.$$

[4] MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

124. Ionization Constants of Weak Electrolytes. — In solutions of weak electrolytes, sufficiently dilute so that inter-ionic forces are negligible, the relationship known as the *Law of Mass Action* holds for the ionized and un-ionized portions of the solute. This law states that the product of the concentrations of the ions, divided by the concentration of the un-ionized portion, gives a value which is sensibly a constant for any given temperature, the ion concentrations being raised to powers equal to the respective numbers of ions of each kind furnished by one mole of the solute. Each weak electrolyte has its own characteristic constant.

Let us take the case of acetic acid as an example. Its ionization can be represented thus,
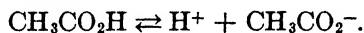
$$CH_3CO_2H \rightleftarrows H^+ + CH_3CO_2^-.$$

Hence, according to the law of mass action, we should have the following relationship satisfied for dilute solutions, namely,

$$\frac{[H^+]\,[CH_3CO_2^-]}{[CH_3CO_2H]} = K,$$

where K is termed the ionization constant of the acid.

The following figures shown in Table 20, which are derived from

Table 20

THE IONIZATION CONSTANT OF ACETIC ACID

C	K	C	K
1.113×10^{-4}	1.778×10^{-5}	9.8412×10^{-3}	1.832×10^{-5}
2.184×10^{-4}	1.781×10^{-5}	5.0000×10^{-2}	1.849×10^{-5}
1.0283×10^{-3}	1.797×10^{-5}	1.0000×10^{-1}	1.846×10^{-5}
5.9115×10^{-3}	1.823×10^{-5}		

measurements by MacInnes and Shedlovsky,[5] give the values of K for different concentrations, C, of acetic acid at 25°.

It should be observed that as the concentration of acid is increased the value of K increases slightly. This effect, known

[5] MacInnes and Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1429 (1932).

as a *salt effect*, is brought about by an increase of the concentration of electrical charge in the solution.   In analysis, changes in concentration of electrical charge and also hydration effects resulting in changes in the value of K make it difficult to carry out accurate calculations involving K.   Nevertheless, it is valuable, in studying the important features of a quantitative analysis, to carry out rough calculations in which these variations in K are neglected.

Table 21

IONIZATION CONSTANTS OF WEAK ELECTROLYTES

Electrolyte	Formula	Temperature	K_1	K_2	K_3
Ammonium hydroxide........	NH_4OH	25°	1.8×10^{-5}		
Acetic acid.......	CH_3CO_2H	"	1.8×10^{-5}		
Boric acid.	H_3BO_3	"	5.8×10^{-10}		
Carbonic acid....	H_2CO_3	"	4.4×10^{-7}	5.6×10^{-11}	
Formic acid......	HCO_2H	"	1.8×10^{-4}		
Hydrocyanic acid.	HCN	"	7.2×10^{-10}		
Hydrogen sulfide..	H_2S	"	9×10^{-8}	1.2×10^{-15}	
Phosphoric acid...	H_3PO_4	"	7.5×10^{-3}	6.2×10^{-8}	5×10^{-13}
Sulfurous acid....	H_2SO_3	"	1.2×10^{-2}	5×10^{-6}	
Tartaric acid (d)..	$H_2C_4H_4O_6$	"	1.0×10^{-3}	4.5×10^{-5}	

The values of K given in Table 21, are those obtained when the salt effect is negligible.   It should be mentioned that these values increase with an increase in temperature.

When it is required to carry out more accurate calculations involving the law of mass action, account must be taken of the effect which concentration of electrical charge has on the equilibrium of the ions and molecules involved.   This can be done by multiplying each concentration by an appropriate factor, f, known as an *activity coefficient*.   The product of a concentration and its activity coefficient is known as an *activity* and is represented by a. By using activities instead of concentrations in the mass action law equation, we have for acetic acid,

$$\frac{([H^+]f_{H^+})([CH_3CO_2^-]f_{CH_3CO_2^-})}{([CH_3CO_2H]f_{CH_3CO_2H})} = \frac{a_{H^+} \times a_{CH_3CO_2^-}}{a_{CH_3CO_2H}} = K$$

where f_{H^+}, $f_{CH_3CO_2^-}$ and $f_{CH_3CO_2H}$ are the activity coefficients of the hydrogen ion, the acetate ion and the un-ionized acetic acid, respectively.   Values of K determined in this manner will be constant with varying concentrations of electrical charge.   The methods used in determining the values of activity coefficients are described in textbooks such as Getman and Daniels and Taylor's Treatise.[6]   In succeeding discussions involving the law of mass action, concentrations will be used except where the use of activities is specifically indicated.

Applying the law of mass action to the ionization of a dibasic acid, let us consider the case of hydrogen sulfide.   It can be shown [7] that for the primary ionization of H_2S:

$$H_2S \rightleftarrows H^+ + HS^-$$
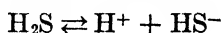
at equilibrium we have

$$\frac{[H^+][HS^-]}{[H_2S]} = 9 \times 10^{-8},$$

and it can also be shown[8] that for the secondary ionization,

$$HS^- \rightleftarrows H^+ + S^=,$$
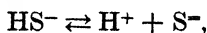
we have

$$\frac{[H^+][S^=]}{[HS^-]} = 1.2 \times 10^{-15}.$$

By multiplying these two equations together, we get a third equation which represents the relationship between the concentrations of hydrogen ion, sulfide ion and un-ionized hydrogen sulfide:

$$\frac{[H^+]^2[S^=]}{[H_2S]} = 1.1 \times 10^{-22}.$$

125. Calculation of Ion Concentrations from Ionization Constant. — For a solution of acetic acid in water, we have the relationship

$$\frac{[H^+][CH_3CO_2^-]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}.$$

[6] Getman and Daniels, "Outlines of Theoretical Chemistry," John Wiley and Sons, Inc., New York, 1937; Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Company, New York, 1931.

[7] Z. physik. Chem., **49**, 220 (1904).

[8] Knox, Trans. Faraday Soc., **4**, 43 (1908).

Let $C =$ the total concentration of acetic acid and let $X =$ [H$^+$]. Since acetate ions and hydrogen ions are formed in equal numbers in the ionizing of acetic acid, it follows that

$$X = [\text{H}^+] = [\text{CH}_3\text{CO}_2^-].$$

When X moles per liter of H$^+$ and CH_3CO_2^- form, X moles of $\text{CH}_3\text{CO}_2\text{H}$ must ionize, hence the remaining concentration of un-ionized molecules of acetic acid is $C - X$.
Substituting, we have,

$$\frac{X^2}{C - X} = 1.8 \times 10^{-5}$$

In a 0.1 M solution, we would have

$$\frac{X^2}{0.1 - X} = 1.8 \times 10^{-5}$$

whence $X = [\text{H}^+] = [\text{CH}_3\text{CO}_2^-] = 0.0013$ moles per liter,
also, $[C - X] = [\text{CH}_3\text{CO}_2\text{H}] = 0.0987$ moles per liter.
The fraction ionized, represented by α, would be

$$\alpha = \frac{0.0013}{0.1} = 0.013,$$

and expressed in per cent, would be $0.013 \times 100 = 1.3\%$.

When the difference between C and $C - X$ is small enough to be neglected, the above calculation of ion concentrations can be simplified. We can say that

$$\frac{X^2}{C} = \frac{X^2}{0.1} = 1.8 \times 10^{-5}$$

in which $X = 0.0013$.

126. The Common Ion Effect. — If to a solution of acetic acid we add sodium acetate, we will increase the concentration of the acetate ion. As a result, we will repress the concentration of hydrogen ion by tying up some of it in the form of undissociated acid with some of the acetate ion which we have added. When equilibrium is established, the following relationship holds:

$$\frac{[\text{H}^+]\,[\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]} = K$$

The contents of Table 22, adapted from the results of Cohn,[9] give verification of the above.

Table 22

Composition of Solution	Conc. of Acetate Ion Due to Sodium Acetate	Conc. of Acetate Ion Due to Acetic Acid	Conc. of H Ion Due to Acetic Acid	Conc. of Undissociated Acetic Acid
0.18 M HAc 0.02 M NaAc	0.02000	0.00022	0.00022	0.17978
0.16 M HAc 0.04 M NaAc	0.04000	0.00010	0.00010	0.15989
0.10 M HAc 0.10 M NaAc	0.10000	0.00003	0.00003	0.09997

The concentration of hydrogen ion in 0.18 M acetic acid is about 1.7×10^{-3}. We see from the above table that the presence in this solution of 0.02 moles per liter of sodium acetate will diminish the hydrogen ion concentration to about one eighth of its former value. The concentration of hydrogen ion in 0.10 M acetic acid of about 1.3×10^{-3} is diminished to about one forty-third of that value by the presence of a concentration of 0.10 moles per liter of sodium acetate.

In a similar manner, the acetate ion concentration in a solution of acetic acid can be repressed by adding HCl. This repression of one of the ions of a weak electrolyte by adding a strong electrolyte having an ion in common is known as the *Common Ion Effect*.

As a further illustration of this effect, let us consider a solution of hydrogen sulfide. Addition of HCl will repress the sulfide ion concentration. By adding a base and thereby diminishing the hydrogen ion concentration, we can bring about a further ioni-

[9] Cohn, *J. Am. Chem. Soc.*, **50**, 696 (1928).

zation of H_2S and an increase in the sulfide ion concentration. Knox has calculated the distribution of the several components which are in equilibrium in the case of hydrogen sulfide, namely:

Undissociated $H_2S \rightleftarrows$ hydrosulfide ion $HS^- \rightleftarrows$ sulfide ion S^-

and showed the relationship given in Table 23.

Table 23

REGULATION OF SULFIDE ION CONCENTRATION BY MEANS OF HYDROGEN ION

Solution	Respective Concentrations at 25°			
	H^+	S^-	HS^-	Undiss. H_2S
Saturated aqueous H_2S..	0.9×10^{-4}	1.2×10^{-15}	0.95×10^{-4}	0.1
Sat. H_2S + 1 M Acetic acid................	4.2×10^{-3}	0.65×10^{-18}	2.1×10^{-6}	0.1
Sat. H_2S + 1 M HCl....	1	1.1×10^{-23}	0.91×10^{-8}	0.1

Since we can regulate the acidity or alkalinity of solutions at pleasure, we thus have a most effective means of controlling the concentration of sulfide ion, a fact which finds most important application in the separation of the metals as sulfides.

In the case of trivalent anions, the same argument applies except that we have one more component to consider in the equilibrium, as represented by the scheme:

Undissociated acid $\rightleftarrows$ monovalent ion $\rightleftarrows$ divalent ion $\rightleftarrows$ trivalent ion

$\longleftarrow$ $\longrightarrow$

in acid solution   in alkaline solution

For the particular case of the phosphate ion, we have

Undissociated $H_3PO_4 \rightleftarrows H_2PO_4^- \rightleftarrows HPO_4^- \rightleftarrows PO_4^{\equiv}$

$\longleftarrow$ $\longleftarrow$

in acid solution   in alkaline solution

The figures for this equilibrium as obtained by Bube [10] from a consideration of the ionization constants of phosphoric acid are

[10] Bube, *Z. anal. Chem.*, **49,** 525 (1911).

given in Table 24.   The total concentration of phosphate in all
forms = 0.01 M.

Table 24

REGULATION OF CONCENTRATIONS OF IONS OF PHOSPHORIC ACID BY MEANS
OF HYDROGEN ION

H^+	H_3PO_4	$H_2PO_4^-$	HPO_4^-	$PO_4^\equiv$
10^{-4}	8.0×10^{-5}	9.9×10^{-3}	2.5×10^{-5}	1.7×10^{-13}
10^{-6}	6.6×10^{-7}	8.1×10^{-3}	2.1×10^{-3}	1.4×10^{-9}
10^{-8}	3.0×10^{-10}	3.8×10^{-4}	9.6×10^{-3}	6.5×10^{-7}
10^{-10}	3.2×10^{-14}	3.9×10^{-6}	9.9×10^{-3}	6.8×10^{-5}

**127. Regulation of Hydrogen Ion Concentration by Means of
Buffers.** — Often in a quantitative analysis there is a change in
the concentration of hydrogen ion brought about by a reaction,
as illustrated herewith by the case of the precipitation of zinc
sulfide:

$$Zn^{++} + H_2S \rightleftarrows ZnS \downarrow + 2H^+.$$
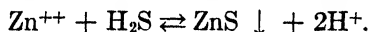
This change, in certain cases, is enough to prevent the reaction
from becoming quantitative, so that provision has to be made
to take care of the hydrogen ions which are formed, in order that
the concentration of hydrogen ion shall remain as constant as
possible during the reaction.   The provision that is generally
resorted to is the use of a *buffer*.   This name is given alike to
the salts of weak acids and to the salts of weak bases and to
mixtures of these with their respective acids or bases.   To illus-
trate buffer action, let us suppose that before passing H_2S into
the solution containing Zn^{++}, we add a considerable quantity
of ammonium formate, thus giving the solution a high concen-
tration of HCO_2^-.   When H_2S is passed into this solution, most
of the H^+ formed, instead of accumulating in the solution, com-
bines with HCO_2^- to form the weak acid HCO_2H.   It is necessary
that the buffer salt be present in an amount relatively large with
respect to the amount of hydrogen ion being generated, so that
the fractional diminution of the buffer ion concentration, due
to the formation of undissociated acid, will be so slight that there
will be only a slight increase in the hydrogen ion concentration.

A quantitative investigation of the buffer action of formate ion was made by Fales and Ware [11] in their study of conditions affecting the precise determination of zinc as the sulfide.[12]   These authors showed that when 1 g. of zinc ammonium sulfate, $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$, was dissolved in 200 ml. of water and the

The Buffer Action of Formate Ion

Formic Mixture Added, ml.	Initial Conc. H^+	Final Conc. H^+
10	$10^{-2.71}$	$10^{-2.25}$
20	$10^{-2.60}$	$10^{-2.35}$
30	$10^{-2.62}$	$10^{-2.35}$
40	$10^{-2.58}$	$10^{-2.35}$

zinc was precipitated as sulfide, the concentration of hydrogen ion increased from $10^{-3.90}$ to $10^{-1.77}$.   When the same amount of zinc was precipitated in a volume of 200 ml. in the presence of varying amounts of a solution, containing, in one liter of solution, 30 ml. of ammonium hydroxide (15 M), 200 ml. of formic acid (23 M), and 250 g. of ammonium sulfate,[13] the initial and final values for the concentration of hydrogen ion were much closer together, as shown in the foregoing tabulation of results.

The portrayal of these results is depicted graphically in Fig. 32.
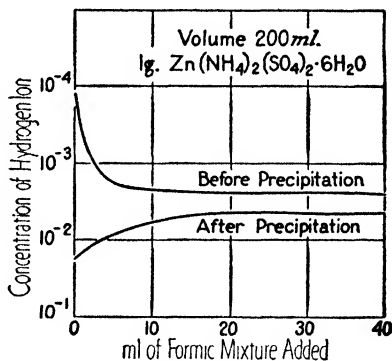
Fig. 32

Buffer Action of Formate Ion

[11] Fales and Ware, *J. Am. Chem. Soc.*, **41**, 490 (1919).

[12] Formic acid is a somewhat stronger acid than acetic, the value of its ionization constant being 0.00021.

[13] The ammonium sulfate was added merely for the purpose of producing a granular precipitate.

In a similar manner, the salt of a weak base, if present in a solution in which OH^- is being formed, will tend to maintain a more nearly constant concentration of OH^-. Ammonium ion furnished by a high concentration of an ammonium salt, such as $(NH_4)_2SO_4$, will combine with most of the OH^- formed to produce undissociated NH_4OH.

128. Calculation of Hydrogen Ion Concentration in Buffered Solutions. — It is sometimes very useful to calculate the concentration of hydrogen ion resulting from the use of a buffer salt in conjunction with its corresponding acid or base. Thus, let it be required to find the concentration of hydrogen ion in a solution which is 0.06 M with respect to acetic acid and 0.2 M with respect to sodium acetate. In this calculation we will neglect the inter-ionic effects mentioned in previous paragraphs. The concentration of the acetate ion due to the sodium acetate can be considered to be 0.2000 M. The concentration of acetate ion due to the acetic acid, which concentration is, of course, equal to the concentration of hydrogen ion from the same source, is unknown, so that we will represent each of these values by X. We then have,

Total concentration of acetate ion $= 0.2000 + X$
Concentration of hydrogen ion $= \quad\ X$
Concentration of undissociated acetic acid $= 0.06 - X$

The corresponding equation is

$$\frac{(0.2000 + X) \times X}{0.06 - X} = 0.000018.$$

Solving this equation we have $X = 0.0_550 = 5.0 \times 10^{-6}$, which is the value of the hydrogen ion concentration.

Since the acetate ion concentration furnished by the acetic acid is very small compared with the total acetate ion concentration, and since the concentration of un-ionized acetic acid is substantially the same as the total concentration of acetic acid, we can simplify the above calculation by saying that

$$\frac{0.2000 \times X}{0.06} = 0.000018$$

where $X = 5.4 \times 10^{-6}$.

This simplified method can be used when the extent of ionization of the weak electrolyte is small in relation to the total concentration of weak electrolyte and of buffer salt.

129. Examples.

1. Calculate the approximate [H^+] of each of the following solutions:

    (*a*) 0.01 *M* HCl

    (*b*) 0.1 *M* CH_3CO_2H

    (*c*) a solution 0.01 *M* with respect to CH_3CO_2H and 0.01 *M* with respect to CH_3CO_2Na

    (*d*) a solution 0.01 *M* with respect to ammonium hydroxide and 0.001 *M* with respect to NH_4Cl

    (*e*) a solution produced by mixing 100 ml. of 0.1 *M* CH_3CO_2H solution and 50 ml. of 0.01 *M* CH_3CO_2Na solution

    (*f*) a solution resulting from the addition of 2 g. of solid NH_4Cl to 100 ml. of 0.03 *M* ammonium hydroxide

2. The equivalent conductances, in reciprocal ohms at 25°, for solutions of sodium acetate, hydrochloric acid and sodium chloride which have the same total ion concentration as the acetic acid are 88.12, 420.41 and 123.25 respectively. When two parallel plates, one centimeter apart and each being one centimeter square, are placed in 0.1 *M* acetic acid at 25°, the resistance between the plates was found to be 1,923 ohms. Calculate the equivalent conductance, the fraction ionized and the ionization constant of the acetic acid.

3. Calculate the approximate [H^+] of a 0.1 *M* solution of H_2S.

4. Solutions (*a*) and (*b*) each have a volume of 100 ml. Solution (*a*) is 1.8 *M* with respect to sodium acetate and 0.1 *M* with respect to acetic acid. Solution (*b*) is 1×10^{-6} *M* with respect to HCl. Calculate the approximate hydrogen ion concentration in each solution.

5. Calculate the approximate hydrogen ion concentration in each solution mentioned in (4) after one milliliter of 0.1 *M* HCl has been added to each. Compare the hydrogen ion concentrations in solutions (*a*) and (*b*) both before and after the addition of the HCl.

6. A buffer solution was prepared by dissolving 0.065 moles of CH_3CO_2H and 0.065 moles of CH_3CO_2Na in one liter of solution. Calculate the approximate [H^+]. What will be the approximate [H^+] after 0.065 moles of HCl are added?

7. Calculate the approximate hydrogen ion concentration in a 0.02 *M* solution of ammonium hydroxide.

CHAPTER VII

ACIDIMETRY-ALKALIMETRY

130. The Ion Product Constant of Water.[1] — It will be advantageous to present a very important relationship which has been established in regard to aqueous solutions, namely, that *in pure water, or in any aqueous solution, whether it is that of an acid, a base, or a salt, there are always present both hydrogen ion and hydroxyl ion, and that whatever the concentration of one, the concentration of the other is such that the product of the two concentrations is a constant for any given temperature*, that is,

$$[H^+][OH^-] = \text{Constant for any given temperature,}$$

or, fixing the temperature at 25°, we have approximately

$$[H^+][OH^-] = 1 \times 10^{-14}.$$

This relationship, which is derivable as a special case of the Law of Mass Action, has been substantiated experimentally by the researches of Arrhenius,[2] Kohlrausch and Heydweiler,[3] Löwenherz,[4] Lorenz and Bohi,[5] Sörensen,[6] and others.

Now it can be seen by virtue of the foregoing relationship that we can define a solution, so far as its acidity or its alkalinity is concerned, either in terms of its concentration of hydrogen ion

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[1] The variation of the ionic product with temperature can be seen from the following figures for pure water, which are taken partly from Kohlrausch and Heydweiler, *Wied. Ann.*, **53**, 209 (1894) and partly from Noyes, *Carnegie Inst. Wash. Pub. No.* **63** (1907):

Temperature	18°	25°	100°
$[H^+][OH^-]$	6.1×10^{-15}	1.1×10^{-14}	4.8×10^{-13}

[2] *Z. physik. Chem.*, **11**, 805 (1893).
[3] *Wied. Ann.*, **53**, 209 (1894).
[4] *Z. physik. Chem.*, **20**, 283 (1896).
[5] *Z. physik. Chem.*, **66**, 733 (1909).
[6] *Biochem. Z.*, **21**, 131 (1909).

or of its concentration of hydroxyl ion, because, the moment we know the value of the one, we impliedly know the value of the other.

Thus consider a 0.1 M solution of hydrochloric acid; at 25° its concentration of hydrogen ion is 10^{-1} or its concentration of hydroxyl ion is 10^{-13} because

$$[OH^-] = \frac{10^{-14}}{[H^+]} = \frac{10^{-14}}{10^{-1}} = 10^{-13}.$$

In an analogous manner, the concentration of hydrogen ion in a 0.1 M solution of sodium hydroxide at 25° is equal to 10^{-13} because the concentration of hydroxyl ion is equal to 10^{-1}.

In order, however, to avoid the disadvantage of a dual system of definition, the convention has been followed of using only the hydrogen ion concentration to characterize a solution irrespective of whether the solution is acid, neutral or alkaline, so that we have for instance,

for 0.1 M HCl, the concentration of hydrogen ion is 10^{-1}
" water itself, "   "   "   "   " " 10^{-7}
" 0.1 M NaOH, "   "   "   "   " " 10^{-13}.

In addition to the exponential form of expressing concentration of hydrogen ion, there is another nomenclature which is in use and which was introduced by Sörensen.[7] In this latter system, the exponent of the activity of the hydrogen ion is used with its negative sign dropped and the symbol pH prefixed, thus,

$$a_{H+} = 10^{-1}, \ pH = 1,$$
$$a_{H+} = 10^{-7}, \ pH = 7,$$
$$a_{H+} = 10^{-13}, \ pH = 13,$$

in which a_{H+} represents the activity of the hydrogen ion. This is equivalent to saying that

$$pH = \log \frac{1}{a_{H+}} = -\log a_{H+}$$

It is often convenient in approximate calculations to use the concentration of hydrogen ion rather than the activity of hydrogen

[7] *Biochem. Z.*, **21**, 159 (1909).

ion in defining pH. In following this practice we can consider that

$$pH = \log \frac{1}{[H^+]} = -\log [H^+]$$

In dealing with pH values, we shall consider that the *concentration* of hydrogen ion is involved rather than the *activity*, except where the activity is specifically indicated.

To illustrate how to change from a given $[H^+]$ to the corresponding pH, let us consider a solution in which $[H^+] = 3.0 \times 10^{-5}$. Then,

$$pH = \log \frac{1}{3.0 \times 10^{-5}} = \log \frac{10^5}{3.0} = \log 10^5 - \log 3.0$$

$$\log 10^5 = 5.00000$$
$$\log 3.0 = 0.47712$$
$$\overline{4.52288}$$
$$\therefore \; pH = 4.52.$$

To change from a pH of 4.52 to the corresponding value of $[H^+]$, we have,

$$pH = 4.52 = \log \frac{1}{[H^+]}$$

eliminating logs $$10^{4.52} = 10^4 \times 10^{0.52} = \frac{1}{[H^+]}$$

or $$3.3 \times 10^4 = \frac{1}{[H^+]}$$

and $$[H^+] = 3.0 \times 10^{-5}.$$

131. Hydrolysis of Salts. — When water reacts with one or more of the ions of a salt, we say that the salt is hydrolyzed, and we describe the reaction as *hydrolysis*. Hydrolysis reactions play a very important part in many quantitative determinations, and it is advisable at this point to consider briefly some of these reactions.

132. *Hydrolysis of a Salt of a Strong Acid and Weak Base.* — When ammonium chloride is dissolved in water, the reaction taking place can be represented by,

$$NH_4^+ + HOH \rightarrow NH_4OH + H^+.$$
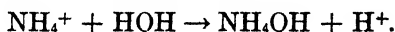
The chloride ion does not react with the water to produce OH^-, and, consequently, the resulting solution is acidic in reaction.

At equilibrium, the following conditions must both be satisfied:

$$[H^+][OH^-] = K_{water}$$

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_{base}$$

Combining these equations by dividing the first by the second, we get

$$\frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{K_{water}}{K_{base}} = K_{hydrolysis}.$$

If we let X represent $[H^+]$, it will represent $[NH_4OH]$ and also the concentration of ammonium ion hydrolyzed. Letting C represent the total concentration of ammonium chloride dissolved in the water, we have

$$\frac{X^2}{C - X} = \frac{K_{water}}{K_{base}}.$$

This expression can be simplified when the difference between C and $C - X$ is negligible, by omitting X from the denominator of the above fraction. This can be done when the extent of hydrolysis is slight. We have then,

$$\frac{X^2}{C} = \frac{K_{water}}{K_{base}}$$

and

$$X = [H^+] = \sqrt{\frac{C \times K_{water}}{K_{base}}}.$$

Using this expression to calculate the $[H^+]$ in a 0.017 M solution of ammonium chloride at 25°, we have

$$[H^+] = \sqrt{\frac{1.7 \times 10^{-2} \times 1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 3.1 \times 10^{-6}$$

and

$$pH = \log \frac{1}{3.1 \times 10^{-6}} = 5.5.$$

The extent of hydrolysis of the NH_4Cl, expressed in per cent, is

$$\frac{3.1 \times 10^{-6} \times 100}{1.7 \times 10^{-2}} = 0.018\%.$$

133. Hydrolysis of a Salt of a Weak Acid and Strong Base. — When sodium acetate is dissolved in water, the reaction taking place can be represented by,

$$CH_3CO_2^- + HOH \rightarrow CH_3CO_2H + OH^-.$$
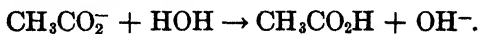
The sodium ion does not react with the water to produce H^+, consequently the resulting solution is basic in reaction. At equilibrium the following conditions both must be satisfied,

$$[H^+] [OH^-] = K_{water}$$

$$\frac{[CH_3CO_2^-] [H^+]}{[CH_3CO_2H]} = K_{acid}.$$

Combining these equations, we have

$$\frac{[CH_3CO_2H] [OH^-]}{[CH_3CO_2^-]} = \frac{K_{water}}{K_{acid}} = K_{hydrolysis}.$$

Letting $X = [OH^-] = [CH_3CO_2H] = $ moles per liter of $CH_3CO_2^-$ hydrolyzed; letting $C = $ the total concentration of sodium acetate dissolved, and, assuming that the difference between C and $C - X$ is negligible, we have

$$\frac{X^2}{C} = \frac{K_{water}}{K_{acid}}$$

and

$$X = [OH^-] = \sqrt{\frac{C \times K_{water}}{K_{acid}}}.$$

Since

$$[H^+] = \frac{K_{water}}{[OH^-]},$$

it follows that $[H^+] = \dfrac{K_{water}}{\sqrt{\dfrac{C \times K_{water}}{K_{acid}}}} = \sqrt{\dfrac{K_{water} \times K_{acid}}{C}}.$

Using this expression to calculate the $[H^+]$ in a 0.017 M solution of sodium acetate at 25°, we have

$$[H^+] = \sqrt{\frac{1 \times 10^{-14} \times 1.8 \times 10^{-5}}{1.7 \times 10^{-2}}} = 3.3 \times 10^{-9}$$

and $pH = \log \dfrac{1}{3.3 \times 10^{-9}} = 8.5.$

Since,

$$[OH^-] = \sqrt{\frac{C \times K_{water}}{K_{acid}}} = \sqrt{\frac{1.7 \times 10^{-2} \times 1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 3.1 \times 10^{-6}$$

the extent of hydrolysis of the CH_3CO_2Na, expressed in per cent is

$$\frac{3.1 \times 10^{-6} \times 100}{1.7 \times 10^{-2}} = 0.018\%.$$

134. *Hydrolysis of a Salt of a Weak Acid and a Weak Base.* — When ammonium acetate is dissolved in water, the reactions which take place may be represented by,

$$NH_4^+ + HOH \rightarrow NH_4OH + H^+$$

$$CH_3CO_2^- + HOH \rightarrow CH_3CO_2H + OH^-.$$
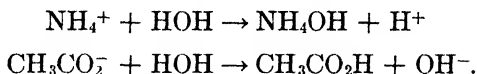
Since both NH_4OH and CH_3CO_2H have substantially the same extent of ionization, these two reactions will proceed to the same extent, and therefore the solution will remain neutral. At equilibrium the following conditions must be satisfied,

$$[H^+][OH^-] = K_{water},$$

$$\frac{[NH_4^+][OH^-]}{[NH_4OH]} = K_{base},$$

$$\frac{[CH_3CO_2^-][H^+]}{[CH_3CO_2H]} = K_{acid}.$$

Dividing the first equation by the product of the other two, we get

$$\frac{[NH_4OH][CH_3CO_2H]}{[NH_4^+][CH_3CO_2^-]} = \frac{K_{water}}{K_{base} \times K_{acid}}.$$

It is apparent that the smaller the value for $K_{base} \times K_{acid}$, the larger will be the value of the fraction and the greater the extent of hydrolysis. When $K_{base} > K_{acid}$, the solution will be basic in reaction and when $K_{base} < K_{acid}$, the solution will have an acidic reaction.

135. *Salts of Strong Acid and Strong Base.* — When $NaCl$ is dissolved in water, the Na^+ does not react with water to liberate H^+, nor does Cl^- react to liberate OH^-. In other words, no hydrolysis takes place and the $[H^+]$ of the solution remains unchanged. In general, salts of a strong base and a strong acid behave in this manner. In solutions of this type we have

$$[H^+] = \sqrt{K_{water}}.$$

136. Titration. — *Acidimetry* deals with the determination of acids by means of bases, while *alkalimetry* deals with the determination of bases by means of acids. The amount of acid in a sample is determined by adding a standard solution of a base until an equivalent quantity of base has been added. From the volume

and concentration of the standard base solution and the chemical
equation involved, the amount of acid present can be calculated.
This addition of an equivalent quantity of a standard solution
is known as *titration*.   In a similar manner, a base can be titrated
by means of a standard acid solution.   The equation involved
in the titration of hydrochloric acid by means of sodium hy-
droxide, is

NaOH : HCl :: Wt. NaOH used : Wt. HCl sought
or   40.01 : 36.47 :: Wt. NaOH used : Wt. HCl sought.
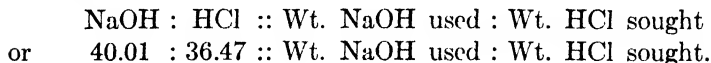
Evidently, in order to be able to make an acid-alkali titration,
we must be able to tell the point at which we have added an
equivalent of base or acid corresponding to the equation involved.
In general, we shall hereafter speak of the point which marks
the addition of an equivalent of reacting substance as the *stoichi-
ometric point* of a reaction, irrespective of whether the reaction
involved is one of neutralization, double decomposition, or oxi-
dation-reduction.   The stoichiometric point is really the theo-
retical point demanded by the equation.

By *end point* of a titration we shall mean the practical point
at which we stop in a titration by virtue of the particular indicator
or other device that is employed.   Our aim in every titration is
to arrange matters so that the end point shall be as nearly coin-
cident with the stoichiometric point as possible.

Let us now consider how we tell the point at which we have
added an equivalent of base or acid corresponding to the stoichi-
ometric equation.   In brief, the location of this point depends
upon the rate at which the concentration of hydrogen ion in the
solution changes value with respect to very small amounts of
alkali (or acid) added as we approach and pass through the
stoichiometric point.   The greater the rate at which the hy-
drogen ion concentration changes,[8] the greater the precision with
which we can locate the stoichiometric point; the more gradual

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[8] Strictly speaking, it is the percentage change and not the absolute change
that is meant.   The graphs which are subsequently given in this chapter,
employing as they do pH as ordinates and milliliters as abscissæ, are in reality
semi-logarithmic plots and consequently rapid change in the value of the
ordinate means rapid percentage change in the concentration of hydrogen (or
hydroxyl) ion.

the change, the less the precision. To illustrate this, we will follow the course of several titrations, plotting the concentration of hydrogen ion as a function of the amount of base (or acid) added.

137. Titration of a Strong Acid with a Strong Base. — First let us consider the titration of hydrochloric acid by means of sodium hydroxide. The reaction taking place can be represented as follows:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + HOH.$$
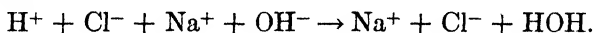
Obviously, at the stoichiometric point we will have virtually a solution of sodium chloride. Since neither Na^+ nor Cl^- undergoes hydrolysis, this solution, if free from impurities, will have a pH of about 7.0. In general, when both acid and base are strong, at the stoichiometric point we have,

$$[H^+] = \sqrt{K_{water}} = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}.$$

Usually CO_2 from the air forms sufficient carbonic acid in solution to make the pH at the stoichiometric point appreciably less than 7.0. Often a pH between 5.8 and 6.0 is observed.

For a solution containing at the start, 25.0 ml. of 0.1 M hydrochloric acid in a volume of 125 ml., we have the following concentrations of hydrogen ion corresponding to the number of milliliters of 0.1 M sodium hydroxide solution added; the temperature being 25°:

ml. 0.1 M NaOH Added	Value of pH	ml. 0.1 M NaOH Added	Value of pH
none	1.75	25.0	6.50
5.0	1.78	25.2	9.00
10.0	1.90	25.5	9.60
15.0	2.05	26.0	9.90
20.0	2.29	26.5	10.10
22.5	2.52	27.5	10.45
23.5	2.77	30.0	10.70
24.0	2.90	35.0	10.90
24.5	3.05	40.0	11.10
24.8	4.00		

These results are shown graphically in Figure 33.   We notice that at first there is an interval where the change in the concentration of hydrogen ion is more or less gradual, then there is a very short interval wher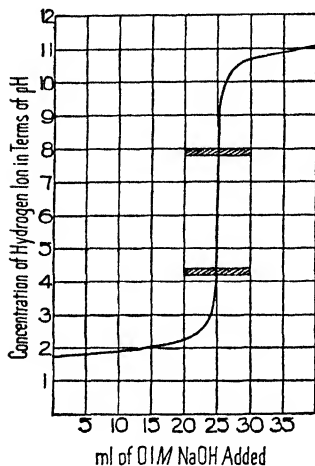e the change takes place very rapidly with respect to very small amounts of sodium hydroxide solution added, after which there is a third interval where the change takes place very slowly again.

Fig. 33

Titration of Hydrochloric Acid with Sodium Hydroxide Solution

The interval of abrupt change is the one that we are particularly interested in, because experiment shows, in general, that whenever we get a point of inflection in the hydrogen ion curve of the titration of a strong acid and strong base, and the element of the curve through the point of inflection is sensibly parallel to the hydrogen ion axis, then the point of inflection corresponds to a stoichiometric point.[9] The form of the titration curve and the coincidence of its point of inflection with the stoichiometric point can be predicted by calculations based on the concentrations and volumes of acid and base used.[10]

We can now lay down the necessary conditions for any acid-alkali titration.   They are:

1. The hydrogen ion curve must show a point of inflection such that the element of the curve through the point of inflection is sensibly parallel to the hydrogen ion axis.

2. The point of inflection must correspond closely to a stoichiometric point.

3. We must be able to locate the point of inflection.

[9] As will be shown later on in the chapter, the converse of this proposition is not always true because there are stoichiometric points for which there are no points of inflection.

[10] P. S. Roller, *J. Am. Chem. Soc.*, **50**, 1 (1928).

If a titration furnishes a curve of the type mentioned, it follows that we will know that we have located the point of inflection if we can tell when the concentration of hydrogen ion in the solution is passing through any of the values included by the element of the curve which is sensibly parallel to the hydrogen ion axis. Thus, for the titration under discussion, we will know that we have located the point of inflection and hence the stoichiometric point, if we can tell when the concentration of hydrogen ion in the solution has any one of the values lying between $10^{-4.0}$ and $10^{-9.0}$, because every value of the concentration of hydrogen ion within this range corresponds to an amount of alkali added which is sensibly the same as that required at the stoichiometric point.

There are two ways of telling when the concentration of hydrogen ion in a solution being titrated has reached a certain value: (1) by use of the hydrogen electrode; (2) by means of the proper indicator.

The hydrogen electrode is not very widely used in titrations, its drawbacks being the elaborate set-up of apparatus that is required and the length of time necessary to make a determination. J. H. Hildebrand,[11] however, describes a simplified arrangement which overcomes these drawbacks to a large extent, and which was used by him in a detailed study of certain titrations. The hydrogen electrode method cannot be conveniently discussed at this point. It will be considered in Chapter XXIV.

The indicators used for measuring hydrogen ion concentration are organic substances, whose very dilute solutions [12] undergo a pronounced change of color as we depart very slightly on either side from some definite concentration of hydrogen ion characteristic of the particular indicator being employed. Thus, a solution containing methyl orange is pink at a concentration of hydrogen ion equal to $10^{-4.2}$ but is faint yellow at $10^{-4.4}$; while with phenolphthalein a solution will be colorless at a concentra-

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[11] J. H. Hildebrand, *J. Am. Chem. Soc.*, **35**, 847 (1913). See also Kolthoff and Furman, "Potentiometric Titrations," for reference see § 11.

[12] Usually three or four drops of a 0.002–0.004 *M* solution are employed per 100 ml. of solution being titrated, depending upon the particular indicator used.

tion of hydrogen ion equal to $10^{-7.8}$ but pink at $10^{-8.0}$. The region of color change of these two indicators is shown in Figure 33 by the lower and upper bands, respectively. Suppose now that we had applied either one of these indicators to the titration under discussion; it is evident that if methyl orange had been used, we would have stopped the titration when about 24.98 ml. of the sodium hydroxide solution had been added, while for phenolphthalein we would have added 25.02 ml.; to reach the stoichiometric point, however, 25 0 ml. are needed. This difference between the stoichiometric point and either one of the end points as given by the above indicators illustrates why it is necessary to distinguish between the stoichiometric point and the end point of a reaction. In general, it is true that for any titration there is more or less of a difference between the stoichiometric point and the end point, and hence it follows that an error of greater or less magnitude is always introduced. If this difference is small in comparison with the total number of milliliters used in the titration, the error will almost disappear when the results are computed by the usual method of ratios (§ 56); if the difference is large, its magnitude must be determined separately and a correction applied. In the above titration this difference is small, being less than one part per thousand.

In the titration of a strong acid with a strong base the approximate pH at various points throughout the titration can be calculated from the excess of acid or base present in the solution and the volume of the solution. From the pH values and the volumes of solution added an approximate titration curve can be constructed.

138. *Titration of a Weak Acid with a Strong Base.* — As a second case, let us consider the titration of the weak acid, acetic acid, with the strong base, sodium hydroxide. In a titration of this type the change in the concentration of the hydrogen ion in the vicinity of the stoichiometric point is less abrupt than it is when both acid and base are strong. This is illustrated in Figure 34 by the curve obtained when 25.00 ml. of 0.1 *M* acetic acid, diluted to 125 ml. is titrated with 0.1 *M* sodium hydroxide solution at 25°. The curve shows pH plotted against milliliters of sodium hydroxide solution added.

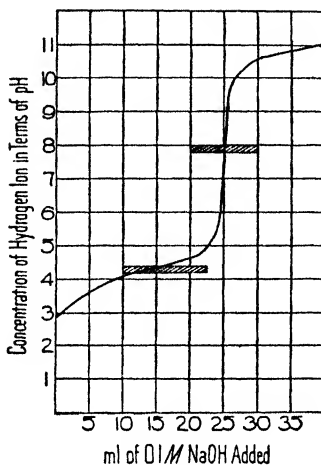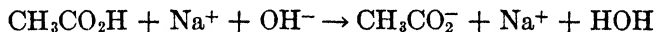| ml. 0.1 M NaOH Added	Value of pH
none	2.86
5.0	3.60
10.0	4.10
15.0	4.35
20.0	4.62
21.0	4.70
22.0	4.85
23.0	5.10
24.0	5.50
24.5	6.00
25.0	7.80
25.5	9.20
26.0	9.80
27.0	10.10
28.0	10.30
30.0	10.63

Fig. 34

Titration of Acetic Acid with Sodium Hydroxide Solution

In this titration the reaction taking place can be represented as follows:

$$CH_3CO_2H + Na^+ + OH^- \rightarrow CH_3CO_2^- + Na^+ + HOH$$

At the stoichiometric point we can consider that we have virtually a solution of sodium acetate. Since the Na^+ of this solution is not hydrolyzed, whereas the $CH_3CO_2^-$ is hydrolyzed according to the reaction,

$$CH_3CO_2^- + HOH \rightarrow CH_3CO_2H + OH^-,$$
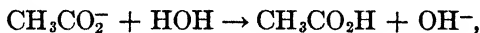
it is obvious that the stoichiometric point will occur in an alkaline solution. We will have at the stoichiometric point a 0.017 M solution of sodium acetate and if this solution is free from impurities we have, as shown in § 133,

$$[H^+] = \sqrt{\frac{K_{water} \times K_{acid}}{C}} = \sqrt{\frac{1 \times 10^{-14} \times 1.8 \times 10^{-5}}{1.7 \times 10^{-2}}} = 3.3 \times 10^{-9}$$

and the pH = 8.5. If CO_2 from the atmosphere is present the pH at the stoichiometric point will have a slightly lower value.

In titrations of this type, it can be shown by means of calculations based on K_{water}, K_{acid} and the concentrations and volumes of the solutions of acid and base, that the point of inflection and the stoichiometric point do not exactly coincide.[13] The difference in pH between these two points can be calculated from the following relationship, where C represents the stoichiometric concentration of the salt at the stoichiometric point,

$$pH_s - pH_t = 0.65 \sqrt{\frac{K_{water}}{C \times K_{acid}}}.$$

It is obvious that the weaker the acid and the less concentrated the solution, the greater the difference between these points. It can be shown [14] that the curve will show a point of inflection only when

$$\frac{K_{water}}{C \times K_{acid}} < 10^{-1.42}.$$

At 25°,

$$K_{water} = 1 \times 10^{-14}$$

and hence we must have,

$$C \times K_{acid} > 1 \times 10^{-12.58}$$

for the curve to show a point of inflection. It is seen from this relationship, that it is undesirable to use excessively dilute solutions of either acid or base as this will result in excessive dilution of the salt at the stoichiometric point and, hence, a less distinct point of inflection and a greater difference between the point of inflection and the stoichiometric point. Thus, the titration of a weak acid with 0.1 M sodium hydroxide solution is preferable to its titration with 0.01 M sodium hydroxide. Likewise, excessive addition of water before titration is to be avoided. It should be borne in mind, however, that if the solution used in titration is very concentrated, the error in overshooting the end point may more than offset the decrease in the error resulting from the difference between the pH at the point of inflection and that at the stoichiometric point. We also observe from the

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[13] For a detailed discussion of this topic see P. S. Roller, *J. Am. Chem. Soc.*, **50**, 1 (1928).

[14] P. S. Roller, *ibid.*, **54**, 3485 (1932).

foregoing relationship that in order to obtain a point of inflection when C is 0.1, K_{acid} must be greater than $10^{-11.58}$. In practice, however, in order to obtain precise results, it is necessary when titrating with 0.1 M acid, that K_{acid} be larger than 10^{-9}. In the foregoing titration of acetic acid with sodium hydroxide the curve will have a point of inflection, since,

$$C \times K_{acid} = 1.7 \times 10^{-2} \times 1.8 \times 10^{-5} = 3.06 \times 10^{-7} > 1 \times 10^{-12\,58}.$$

The difference in pH between the stoichiometric point and this point of inflection will be given by the following:

$$pH_s - pH_i = 0.65 \sqrt{\frac{1 \times 10^{-14}}{1.7 \times 10^{-2} \times 1.8 \times 10^{-5}}} = 1.2 \times 10^{-4}\,pH$$

which produces a negligible error in the titration.

In the titration just considered, the difference between end point and stoichiometric point is brought out very strongly if methyl orange is used as the indicator. As shown in Figure 34, the end point with this indicator takes place at 17.0 ml. of sodium hydroxide solution added, while the stoichiometric point is at 25.0 ml. This corresponds to an error of 320 parts in 1,000. On the other hand, the end point with phenolphthalein is sensibly the same as the stoichiometric point.

In the titration of a weak acid with a strong base the approximate hydrogen ion concentration can be calculated at various points prior to the stoichiometric point from the ionization constant of the acid. Thus, in the case of acetic acid we have

$$[H^+] = \frac{[CH_3CO_2H]\,K_{acid}}{[CH_3CO_2^-]}.$$

At the stoichiometric point it can be obtained from

$$[H^+] = \sqrt{\frac{K_{acid} \times K_{water}}{C}}$$

and after the stoichiometric point has been passed it can be obtained from the excess base present and the volume of the solution. From the values of the hydrogen ion concentration at various stages of the titration the corresponding pH values

can be calculated. From the pH values and the volumes of solution added, an approximate titration curve can be plotted.
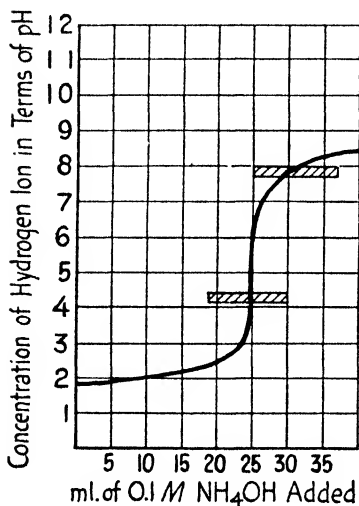

Fig. 35

Titration of Hydrochloric Acid with Ammonium Hydroxide Solution

In a similar manner the curve for the titration of a strong acid with a weak base can be obtained.

139. *Titration of a Strong Acid with a Weak Base.* — When we titrate a strong acid with a weak base, the change in the concentration of hydrogen ion in the vicinity of the stoichiometric point is less abrupt than it is when the acid is titrated with a strong base. This is illustrated in Figure 35 by the curve obtained when 25.00 ml. of 0.1 M hydrochloric acid, diluted to 125 ml., is titrated with 0.1 M ammonium hydroxide at 25°. The curve shows pH plotted against milliliters of ammonium hydroxide solution added.

The reaction taking place can be represented as follows:

$$NH_4OH + H^+ + Cl^- \rightarrow NH_4^+ + Cl^- + HOH.$$
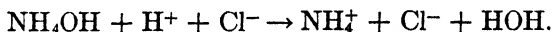
At the stoichiometric point we will have virtually a 0.017 M solution of ammonium chloride. Since Cl^- is not hydrolyzed whereas NH_4^+ is hydrolyzed according to the reaction

$$NH_4^+ + HOH \rightarrow NH_4OH + H^+,$$
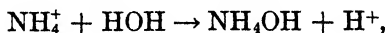
it is obvious that the stoichiometric point will occur in an acid solution. If this solution is free from impurities we have as shown in § 132,

$$[H^+] = \sqrt{\frac{C \times K_{water}}{K_{base}}} = \sqrt{\frac{1.7 \times 10^{-2} \times 1.0 \times 10^{-14}}{1.8 \times 10^{-5}}} = 3.1 \times 10^{-6}$$

and the pH = 5.5. If CO_2 from the atmosphere is present in

[178]

the solution, the pH at the stoichiometric point will have a slightly lower value.

In titrations of this type it can be shown that the point of inflection of the titration curve does not exactly coincide with the stoichiometric point. The difference in pH between these two points is given by the following equation, where C is the stoichiometric concentration of salt at the stoichiometric point,

$$\text{pH}_s - \text{pH}_i = 0.65 \sqrt{\frac{K_{\text{water}}}{C \times K_{\text{base}}}}.$$

Obviously, the weaker the base and the less concentrated the solution, the greater will be the difference between these points. It can be shown that when

$$\frac{K_{\text{water}}}{C \times K_{\text{base}}} < 10^{-1 \, 42}$$

no point of inflection will appear. In the foregoing titration of hydrochloric acid with ammonium hydroxide, the point of inflection falls very close to the stoichiometric point so that the error resulting from the difference between these points is negligible.

If phenolphthalein is used as the indicator for this titration it will change color at about 30 ml. whereas the stoichiometric point is reached by the addition of 25.0 ml. of solution. This corresponds to an error of 200 parts per 1,000. On the other hand, the end point of methyl orange is very close to the stoichiometric point and, consequently, the error involved by its use is very small.

140. *Titration of a Weak Acid with a Weak Base.* — As a concluding case for the monobasic acids, let us take up the one where the change in the concentration of hydrogen ion at the stoichiometric point is so gradual that it cannot be used to locate the stoichiometric point. This is the case when both the acid and the base are weakly ionized, as evidenced by the graph in Figure 36 which gives the results of adding ammonium hydroxide to acetic acid. Thus we have the following concentrations of hydrogen ion corresponding to the number of milliliters of 0.1 M ammonium hydroxide added to a solution containing at the start

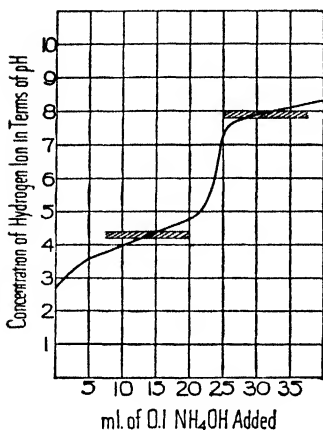25.0 ml. of 0.1 M acetic acid in a volume of 125 ml., the temperature being 25°:

Fig. 36

Titration of Acetic Acid with
Ammonium Hydroxide Solution

ml. 0.1 M NH$_4$OH Added	Value of pH
none	2.7
5.0	3.6
10.0	4.0
15.0	4.4
20.0	4.8
21.0	4.9
22.0	5.1
23.0	5.5
24.0	6.3
25.0	7.3
26.0	7.6
27.0	7.7
30.0	7.9
35.0	8.1
40.0	8.3

In titrations of this type the error involved in locating the stoichiometric point is very large. In the above titration, when phenolphthalein is used as the indicator this error is about 167 parts per 1,000. In general, the smaller the ionization constants of acid and base and the greater the dilution of the solution at the stoichiometric point, the greater the difficulty in locating the stoichiometric point.

141. General Considerations in Titrating with a Base. — Summarizing the behavior of monobasic acids upon neutralization, we may say that if both acid and base are strongly ionized there will be an abrupt change in the concentration of hydrogen ion at the stoichiometric point; if either the acid or the base are feebly ionized, the change will not be so abrupt but it still can be used in many cases to locate the stoichiometric point; if both the acid and base are feebly ionized, the change will be gradual and cannot be used to locate precisely the stoichoimetric point. In other words, titration of a weak acid by means of a weak base, or vice versa, is attended by a large error and should be

avoided.   Table 25 shows the region of abrupt change for the more common monobasic acids when titrating 25.0 ml. of 0.1 M acid in 125 ml. of solution with 0.1 M base.

Table 25

REGIONS OF ABRUPT CHANGE FOR THE MORE COMMON MONOBASIC ACIDS

Acid	Region of Abrupt Change in the Concentration of Hydrogen Ion when the Acid is Titrated with KOH or NaOH
Hydrochloric.........	pH 3.8 — 9.0
Nitric...............	3.8 — 9.0
Formic..............	5.5 — 9.0
Acetic..............	6.5 — 8.5

142. Dibasic Acids. — When we come to dibasic acids we have two stoichiometric points, the first corresponding to the formation of the acid salt, the second corresponding to the formation of the normal salt.   When [15] $C \times K_{1\,acid}, > 10^{-12.58}$ and $K_{1\,acid} > 10^4 \times K_{2\,acid}$, the first stoichiometric point will yield a point of inflection.   For precise titrations to the first stoichiometric point with a strong base, it is necessary that $C \times K_{1\,acid}$ be greater than 1×10^{-10}.   If K_2 is extremely small, a point of inflection may not appear for the second stoichiometric point.   This is the case in the titration of carbonic acid (§ 124).   In the case of sulfurous acid $K_{1\,acid}$ and $K_{2\,acid}$ differ sufficiently and K_2 is sufficiently large so that it is possible to titrate to both stoichiometric points.   In the case of sulfuric acid, the constant for its secondary ionization is large enough to prevent a point of inflection corresponding to the first stoichiometric point and also large enough to give, at ordinary concentrations, a well defined point of inflection corresponding with the second stoichiometric point.   The reactions for titrations of sulfuric acid with sodium hydroxide may be represented by the following equations:

$$H_2SO_4 + NaOH \rightleftarrows NaHSO_4 + H_2O$$
$$H_2SO_4 + 2\ NaOH \rightleftarrows Na_2SO_4 + 2\ H_2O.$$
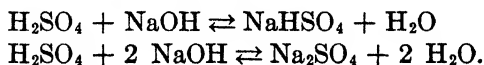
[15] H. T. S. Britton, "Hydrogen Ions," 2nd ed., D. Van Nostrand, Inc., New York, 1932.

When 17.00 ml. of 0.1 M sulfuric acid were made up to 200 ml. with distilled water and titrated with 0.1 M sodium hydroxide solution at 25° the following data [16] were obtained.   The curve for this titration is shown in Figure 37.   We can see from this curve that either methyl orange or phenolphthalein will indicate fairly closely the stoichiometric point at which $H_2SO_4 \equiv 2 NaOH$.
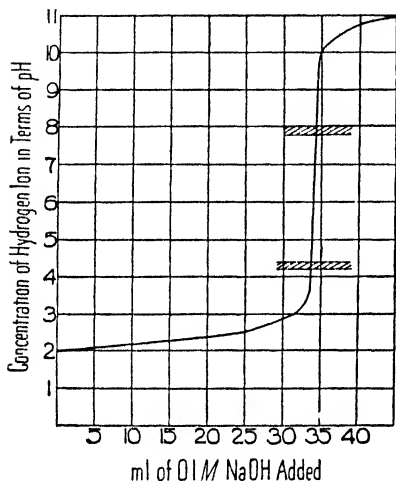

Fig. 37

Titration of Sulfuric Acid with Sodium Hydroxide Solution

ml. 0.1 M NaOH Added	Value of pH
none	2.0
5.0	2.1
10.0	2.2
15.0	2.3
20.0	2.4
25.0	2.6
30.0	2.9
32.0	3.1
33.0	3.4
33.5	3.7
34.0	6.7
34.5	10.0
35.0	10.1
36.0	10.3
37.5	10.5
40.0	10.8
45.0	11.0
50.0	11.1

The regions of abrupt change for the common dibasic acids when titrating 25.0 ml. of 0.1 M acid in 125 ml. of solution with 0.1 M base, are given in Table 26.

143. Tribasic Acids. — For tribasic acids we have three stoichiometric points, corresponding respectively to the formation of the primary, secondary, and tertiary salts, but, of the acids so far investigated, no acid shows more than two regions of abrupt change, while some show only one such region, and some show

[16] The author is indebted to Dr. Clarke E. Davis of The National Biscuit Co., New York, N. Y., for his courtesy in supplying this data.

Table 26

REGIONS OF ABRUPT CHANGE FOR THE MORE COMMON DIBASIC ACIDS

| Acid* | Region of Abrupt Change in the Concentration of Hydrogen Ion when Acid is Titrated with KOH or NaOH | |
	1 Equiv. of Base	2 Equivs. of Base
Sulfuric............	none	pH 4.0 − 9.0
Oxalic.............	none	5.0 − 9.0
Succinic...........	none	7.3 − 8.5
Carbonic	pH 7.3 − 8.5	none
Hydrogen sulfide....	....	none
Silicic.............	none	none

* Titration curves for oxalic, malonic, maleic and fumaric acids are by Hildebrand; for reference see § 137; that for succinic acid by C. E. Davis, E. T. Oakes and H. M. Salisbury, *Ind. Eng. Chem.*, **15**, 182 (1923).

none at all, as can be seen by reference to Table 27. These regions of abrupt change were determined by titrating 0.1 *M* acid in 125 ml. of solution with 0.1 *M* base.

Table 27

REGIONS OF ABRUPT CHANGE FOR SOME TRIBASIC ACIDS

| Acid | Region of Abrupt Change in the Concentration of Hydrogen Ion when Acid is Titrated with KOH or NaOH | | |
	1 Equiv. of Base	2 Equivs. of Base	3 Equivs. of Base
Citric [17]........	none	none	pH 7.0 − 8.5
Phosphoric.....	pH 3.8 − 5.0	pH 7.5 − 9.0	none
Boric..........	none	none	none
Arsenious......	none	none	none

[17] The titration curve for citric acid is given by Hildebrand, reference given in § 137; also by C. E. Davis, E. T. Oakes, and H. M. Salisbury, reference given in § 142.

144. *Titration of Phosphoric Acid.* — The curve for phosphoric acid is given in Figure 38. The first point of inflection happens exactly at the first stoichiometric point. The second point of inflection only approximately indicates the second stoichiometric point; there is no third point of inflection. The data for the curve were obtained by diluting 25.00 ml. of 0.0333 M phosphoric acid to a volume of 125 ml., and then titrating with 0.1 M sodium hydroxide solution, the temperature being 25°:
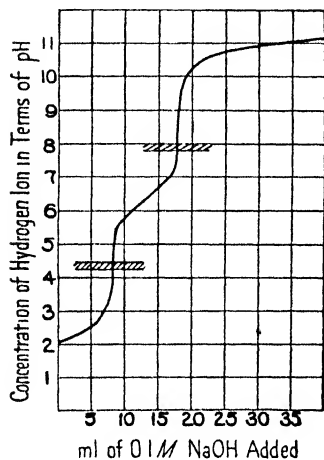
Fig. 38

Titration of Phosphoric Acid with Sodium Hydroxide Solution

ml. 0.1 M NaOH Added	Value of pH
none	2.1
5.0	2.6
6.0	2.7
7.0	3.1
7.5	3.3
8.0	3.5
8.5	5.1
9.0	5.5
11.0	6.0
13.0	6.4
15.0	6.7
17.0	7.2
17.5	7.5
18.0	9.2
19.0	10.0
21.0	10.4
23.0	10.6
25.0	10.8
27.5	10.9
30.0	11.0
35.0	11.1

Since methyl orange changes color very near the first stoichiometric point, it can be used to indicate the following relationship,

$$H_3PO_4 \equiv NaOH.$$
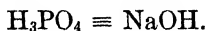
Phenolphthalein changes near the second stoichiometric point and so it can be used to indicate approximately the relationship,

$$H_3PO_4 \equiv 2 NaOH.$$

[184]
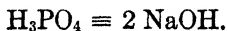
145. *Titration of Boric Acid.* — If boric acid is titrated in aqueous solution, the curve shows no point of inflection, but, if mannite is added to the boric acid solution in considerable quantity, a curve is obtained which exhibits a point of inflection corresponding to the addition of one equivalent of NaOH. The mannite appears to form a complex with the boric acid, which is more highly ionized than the boric acid itself. Invert sugar, glucose, glycerol, and other polyhydric alcohols produce similar effects.

146. Titration of Bases by Means of Acids. — The principles that apply to the titration of acids likewise apply to the titration of bases; we get an abrupt change in the hydrogen ion concentration at the stoichiometric point, provided that we use an acid which is strongly ionized, as shown in Figure 39, which gives the graph for the titration of sodium hydroxide by means of hydrochloric acid, when 25.0 ml. of 0.1 M sodium hydroxide was diluted to 125 ml. and then titrated with 0.1 M hydrochloric acid, the temperature being 25°.

ml. 0.1 M HCl Added	Value of pH
none	11.1
5.0	11.0
10.0	10.9
15.0	10.7
20.0	10.3
22.5	9.9
23.5	9.6
24.0	9.4
24.5	9.1
24.8	8.7
25.0	6.0
25.2	3.5
25.5	3.0
26.0	2.7
26.5	2.6
27.5	2.4
30.0	2.2
35.0	2.0
40.0	1.9
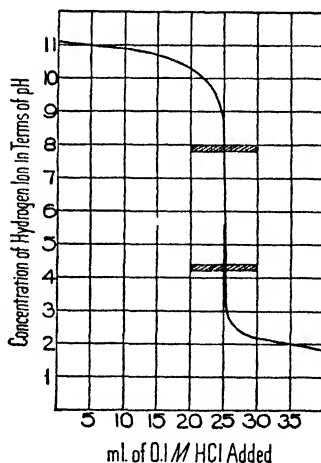
Fig. 39

Titration of Sodium Hydroxide with Hydrochloric Acid

[185]

When 25.0 ml. of 0.1 M ammonium hydroxide in 125 ml. of solution is titrated with 0.1 M hydrochloric acid, the curve obtained makes it evident that phenolphthalein will not give an accurate end point, whereas the end point indicated by methyl orange is very close to the stoichiometric point. The curve for this titration is shown in Figure 40.
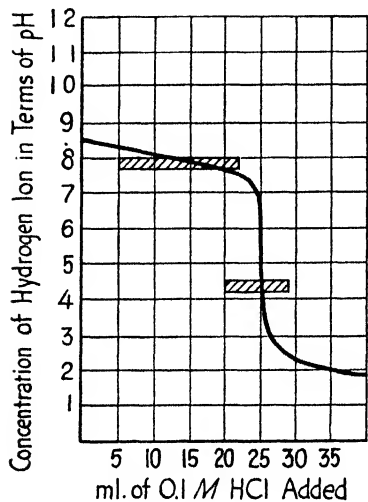

Fig. 40

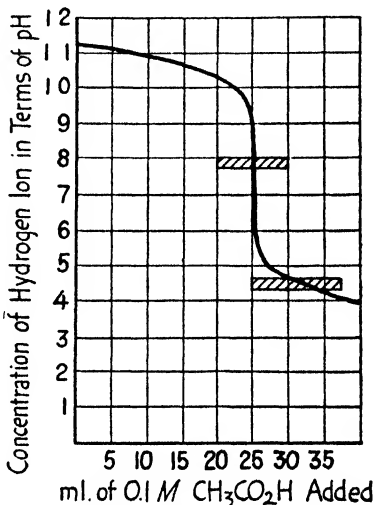Titration of Ammonium Hydroxide with Hydrochloric Acid

Fig. 41

Titration of Sodium Hydroxide with Acetic Acid

When 25.0 ml. of 0.1 M sodium hydroxide is titrated with 0.1 M acetic acid, the curve obtained permits of the use of phenolphthalein but not of methyl orange as the indicator. This is shown in Figure 41.

With the di-acid alkalies, barium hydroxide and calcium hydroxide, we get only one region of abrupt change and this corresponds to the addition of two equivalents of monobasic acid. The regions of abrupt change for 25.0 ml. of 0.1 M solutions of the common alkalies, diluted to 125 ml. when titrated with 0.1 M acid, are given in Table 28.

Table 28

REGIONS OF ABRUPT CHANGE FOR COMMON ALKALIES

Base	Region of Abrupt Change in Concentration of Hydrogen Ion when Base is Titrated with a Strongly Ionized Acid	
Potassium hydroxide....	pH 9.0 — 4.0	
Sodium hydroxide......	9.0 — 4.0	
Ammonium hydroxide...	6.0 — 4.0	
	1 Equiv. of Acid	2 Equivs. of Acid
Barium hydroxide......	none	pH 9.0 — 4.0
Calcium hydroxide......	none	9.0 — 4.0

147. Titration of Salts Which Show Hydrolysis. — It is possible to titrate salts by means of acids or bases as the case may be, if the concentration of hydrogen ion in the salt solution undergoes an abrupt change at the stoichiometric point. In order that this change may happen, it is necessary that the concentration of hydrogen ion in the solution of the salt at the start of the titration shall be greater than 10^{-5} if we are using a base to titrate with, or less than 10^{-9} if we are using an acid. Now the concentration of hydrogen ion in a solution of a salt is a function both of the concentration of the salt and of the constitution of the salt. For the concentrations of salt which obtain for the weights of salt and volumes of solution usually employed in volumetric analysis, the concentration of hydrogen ion for different solutions of the same salt does not vary much. For different salts, however, the concentration of hydrogen ion in the solution varies greatly according to the constitution of the salt. As a result of hydrolysis, a solution containing the salt of a strong acid and a weak base will be acid, whereas a solution containing the salt of a strong base and a weak acid will be basic. If the solution contains a salt of a weak base and weak acid, then a basic solution will result if the acid is weaker than the base, and an acidic solution will result if the base is weaker than the acid. Now we have pointed out that, for purposes of

titration, the concentration of hydrogen ion in the salt solution at the start of the titration must be considerably different from 10^{-7}, namely it must be greater than 10^{-5} or less than 10^{-9}. This condition will obtain if the base and the acid are each readily soluble and their ionization constants are of a sufficiently different order of magnitude; indeed, the ionization constant of the one must be about 10^8 times the value of the other. This then limits the titration of salts by means of acids or bases to those cases where the salt is either the salt of a very weak base and a strong acid, or the salt of a strong base and a very weak acid.[18]

148. Salts of Weak Bases and Strong Acids. — Examples of this class are very few, the titration of aniline hydrochloride[19] and aluminum sulfate being about all that are ordinarily encountered. The titration curve for the latter is given in Figure 42; from this it will be noticed that there is a first region of abrupt change corresponding to the stoichiometric point,

$$Al_2(SO_4)_3 + 6\ NaOH \rightarrow 2\ Al(OH)_3 + 3\ Na_2SO_4$$
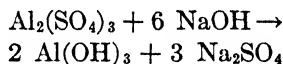
which takes place at a concentration of hydrogen ion lying between $10^{-6.0}$ and $10^{-7.0}$. There is a second region between $10^{-9.5}$ and $10^{-9.8}$ but apparently this does not correspond to any stoichiometric relation.

Fig. 42

Titration of Aluminum Sulfate with Sodium Hydroxide Solution

[18] Strictly speaking, a strong acid or base does not have an ionization constant but, for the purpose in hand, we can assume a value of one as fairly representative of the ionization of a strong acid or base.

[19] Hildebrand, see reference given in § 137.

The data for the curve were obtained by dissolving 0.278 g. of $Al_2(SO_4)_3$ in 125 ml. of water and titrating with 0.1 M sodium hydroxide solution, the temperature being 25°:

ml. 0.1 M NaOH Added	Value of pH	ml. 0.1 M NaOH Added	Value of pH
none	3.5	25.0	8.3
5.0	3.9	27.5	8.9
10.0	4.0	30.0	9.2
15.0	4.0	32.5	9.4
17.5	4.2	33.5	9.4
20.0	4.4	34.0	9.7
22.5	5.2	35.0	10.2
23.0	5.5	37.5	10.7
23.5	6.1	40.0	11.1
24.0	7.7	45.0	11.5
24.5	8.0	50.0	11.7

149. Salts of Strong Bases and Weak Acids. — Examples of this class of salts are more numerous and more frequently encountered. Thus we have the sodium or potassium salts given in Table 29. The regions of abrupt change are those produced when 25.0 ml. of 0.1 M solutions of salt, diluted to 125 ml. are titrated with 0.1 M acid.

Table 29

REGIONS OF ABRUPT CHANGE FOR SOME SODIUM AND POTASSIUM SALTS

Salt	Region of Abrupt Change in Concentration of Hydrogen Ion when Salt is Titrated with HCl, HNO₃, or H₂SO₄	
Sodium or potassium oleate palmitate stearate	Usually assumed to occur at pH 5.0 − 4.0	
	1 Equiv. of Acid	2 Equivs. of Acid
carbonate...........	pH 8.0 − 7.0	pH 4.6 − 3.5

150. *Titration of Sodium Carbonate.* — The case of sodium carbonate is particularly interesting because of the wide application which this salt finds in the standardization of the acids ordinarily used in acidimetry-alkalimetry, namely, hydrochloric, nitric, and sulfuric. The carbonate ion of sodium carbonate is hydrolyzed as follows:

$$CO_3^- + HOH \rightarrow HCO_3^- + OH^-.$$
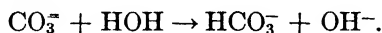
When the solution is titrated with acid, hydroxyl ions are removed from the solution so that eventually the reaction goes to completion. Each carbonate ion in the original solution furnishes an hydroxyl ion. When these hydroxyl ions are titrated with the acid, they serve as a measure of the quantity of carbonate ion originally present. The stoichiometric relationship is

$$Na_2CO_3 \equiv HCl.$$
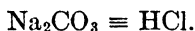
It is to be observed that the first region of abrupt change of the hydrogen ion concentration does not correspond exactly to the addition of one equivalent of acid, but occurs somewhat before this point is reached. Where there is no attempt at a high degree of precision phenolphthalein can be used to indicate the first stoichiometric point.

Bicarbonate ions exhibit a tendency to become hydrolyzed as follows:

$$HCO_3^- + HOH \rightarrow H_2CO_3 + OH^-.$$
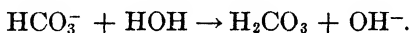
If the titration with acid is continued, this reaction can be made to go to completion. The hydroxyl ions removed in titration serve as a measure of the bicarbonate ions hydrolyzed. The stoichiometric relationship for the second part of this titration is,

$$NaHCO_3 \equiv HCl.$$
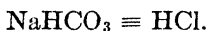
For the entire titration the relationship is,

$$Na_2CO_3 \equiv 2 \ HCl.$$
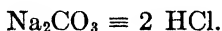
The second region of abrupt change takes place very close to the second stoichiometric point and can be indicated with very little error by means of methyl orange.

The data for the curve of Figure 43 were obtained by dissolving 0.1325 g. of Na_2CO_3 in 125 ml. of water and then titrating with 0.1 M hydrochloric acid at 25°.

| ml. 0.1 M HCl Added	Value of pH
none	10.0
5.0	9.7
7.5	9.3
10.0	8.8
10.5	8.6
11.0	8.4
11.5	8.0
12.0	7.8
12.5	7.0
13.0	6.7
15.0	6.2
20.0	5.5
22.5	5.2
23.5	5.0
24.0	4.9
24.5	4.7
25.0	4.0
25.5	3.0
26.0	2.7
27.5	2.4
30.0	2.2
35.0	2.0
40.0	1.9
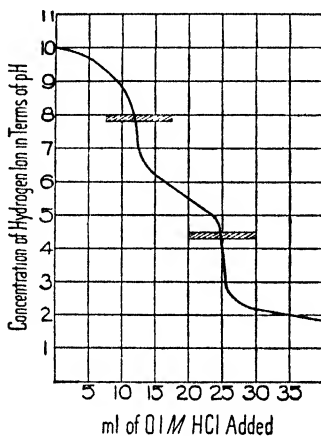
Fig. 43

Titration of Sodium Carbonate with Hydrochloric Acid

151. Differential Titration. — In certain cases it is possible by a proper choice of indicators to determine two constituents in a single titration. A very common example coming under this head is the determination of the respective amounts of sodium hydroxide and sodium carbonate in a mixture of the two. By adding phenolphthalein to a solution containing these substances and titrating with acid until the color of phenolphthalein is just discharged (pH = 7.8), we will have satisfied all the sodium hydroxide and one-half the sodium carbonate according to the reactions:

A $\begin{cases} NaOH + HCl \rightarrow NaCl + H_2O \\ Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl. \end{cases}$

[191]
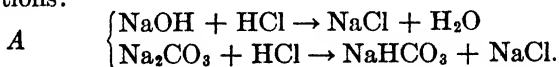
By now adding methyl orange to the solution being titrated and continuing the titration until the methyl orange end point is reached (pH = 4.2), we will have satisfied, according to the equation given below, the sodium bicarbonate formed during the first stage of the titration

$$B \quad NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$
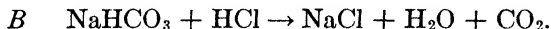
We have thus established the following correspondence:

A gives the milliliters of acid $\equiv$ all $NaOH + \frac{1}{2} Na_2CO_3$,
B " " " " " $\equiv$ $\frac{1}{2} Na_2CO_3$.

Whence by difference $A - B$ gives the milliliters of acid equivalent to the NaOH, and by subtracting this latter number of milliliters from the total number of milliliters of acid used, we obtain the milliliters of acid equivalent to the Na_2CO_3.

By way of illustration, let us suppose that 20.50 ml. of 0.1 M HCl are required to reach the phenolphthalein end point while an additional 5.30 ml. are needed to change the color of methyl orange. The total volume added being 25.80 ml. Then,

$$20.50 \text{ ml. } 0.1 \text{ } M \text{ HCl} \equiv NaOH + \tfrac{1}{2} Na_2CO_3$$
$$\underline{5.30 \text{ ml. } 0.1 \text{ } M \text{ HCl} \equiv \tfrac{1}{2} Na_2CO_3}$$
$$15.20 \text{ ml. } 0.1 \text{ } M \text{ HCl} \equiv NaOH$$

and

$$25.80 \text{ ml.}$$
$$\underline{15.20 \text{ ml.}}$$
$$10.60 \text{ ml. } 0.1 \text{ } M \text{ HCl} \equiv Na_2CO_3.$$

The method of calculation of the actual weight of NaOH and Na_2CO_3 present in the sample will be considered in the following chapter.

It is possible to carry out a differential titration of a solution containing a mixture of acids provided there is sufficient difference between their ionization constants so that when the stoichiometric point for the first acid is reached the second acid is still substantially un-ionized. As in the case of dibasic acids, the constant of the stronger acid must be greater than 10^4 times the constant of the weaker acid when both acids have the same

concentration. The larger the concentration of the second acid with respect to the first, the greater must be the difference in their ionization constants.[20]

152. Indicators. — Indicators used in acid-base titrations are either very weak acids or very weak bases.[21] Their ionization can be represented by the following equations:

$$IndOH \rightleftharpoons Ind^+ \, OH^-$$
$$HInd \rightleftharpoons H^+ \, Ind^-.$$
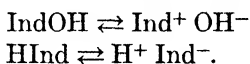
Applying the Law of Mass Action to either of the above equations, it is evident that a change in the concentration of H^+ will cause a displacement of the equilibrium. If solutions of the un-ionized and ionized forms differ in color, then the displacement of the equilibrium can be made to produce a color change in the solution. If we determine experimentally the concentrations of H^+ between which the color of the solution changes, it is possible to use this color change as a guide in the measurement of the concentration of H^+. In selecting an indicator for a titration, it is necessary that the concentrations of H^+, between which the color changes, must fall very close to the stoichiometric point of the titration.

While a suitable choice of either methyl orange or phenol-phthalein will suffice for nearly all cases that admit of titration, there are times when the use of some other indicator is advisable. In particular, the list of indicators advocated and, in major part, developed by Clark & Lubs [22] is to be recommended; this list comprises thymol blue, brom-phenol blue, methyl red, brom-cresol purple, brom-thymol blue, phenol red, cresol red, cresol phthalein, and covers a range of hydrogen ion concentration ranging from pH = 2.0 to pH = 9.2. These indicators, as well as certain others which find application in analytical chemistry, are described in detail in the following list. The values given for the pH range of each indicator are not the extreme range of the

---

[20] Kolthoff and Furman, "Potentiometric Titrations," 2nd ed., p. 38, John Wiley & Sons, Inc., New York, 1931.

[21] For a most thorough and complete treatment of the subject of indicators and a wonderful bibliography in regard to them, the reader is referred to W. M. Clark, "The Determination of Hydrogen Ions," 3rd ed., Williams & Wilkins Co., Baltimore, 1928.

[22] *J. Wash. Acad. Sci.*, **6**, 483 (1916).

indicator, but the least range over which the color change is plainly noticeable to the eye when the amount of indicator specified is used and the volume of the solution which is being observed is 125 to 175 ml. and the observation is made in daylight.

In general, it is to be remarked that the appearance of a color is more easily distinguished than is the disappearance, so that if there is a choice between a one-color indicator and a two-color, the former is to be preferred. Some indicators cannot be used in the presence of salts of the heavy metals; others cannot be used if ammonium salts are present and the solution is to be titrated by means of a strongly ionized base, phenolphthalein being such an indicator.

Of all considerations for analytical purposes, the cardinal one is, as already pointed out, *that the indicator must be so selected that it gives a sharp color change over a very small range of hydrogen ion concentration and within the region where the concentration of hydrogen ion of the solution undergoes its abrupt change.*

153. List of Indicators. — Some of the properties and uses of a number of important indicators will now be considered.

Methyl Violet 6B, Schultz No. 517.[23]
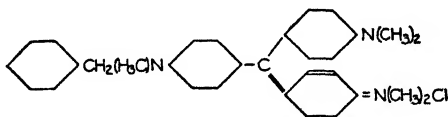
Mol. wt. 484

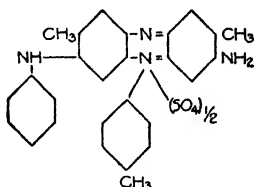0.050 g. in 100 ml. water = 0.001 M. 3–8 drops per 100 ml. solution.

pH = 0.4	pH = 0.6	pH = 1.0
yellow	green	blue

The colors are very fugitive, therefore the indicator does not give very accurate adjustments of pH. It is used in adjusting the concentration of hydrogen ion for the separation of the copper and arsenic groups from the aluminum and zinc groups by means of hydrogen sulfide. The concentration of hydrogen ion for this purpose should lie between $10^{-0.4}$ and $10^{-0.6}$ (equivalent to a concentration of HCl of 0.4 to 0.25 M) depending

[23] By "Schultz No." we shall mean the number given the indicator in "Tabellarische Übersicht der in Handel befindlichen kunstlichen organischen Farbstoffe," by Gustav Schultz and Paul Julius, 5th ed., edited by Gustave Schultz, Berlin, 1914. This work gives very valuable information in regard to the formulas, trade names, literature, etc., of the organic dyes.

upon the relative amounts of the metals present.   For particulars as to
the limits of separation possible under these circumstances, especially as
regards the non-precipitation of small quantities of cadmium or lead, or
the precipitation of some of the zinc along with the copper and arsenic
groups, see Noyes & Bray, *J. Am. Chem. Soc.*, **29**, 137 (1907).

Mauveine or Rosolane, Schultz No. 688.
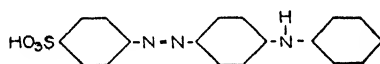
Mol. wt. 513

0.050 g. in 100 ml. water = 0.001 *M*.   3–8 drops per 100 ml. solution.

pH = 1.0   pH = 2.0   pH = 3.0
   green   blue   violet

This indicator is used for the same purpose as Methyl Violet 6B.

Tropaeolin 00, Orange IV, Schultz No. 139.   Diphenylamino-azo-
p-benzene-sulfonic Acid.
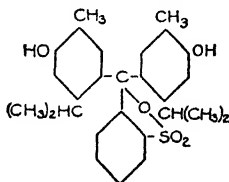
Mol. wt. 353

0.010 g. in 100 ml. water = 0.0003 *M*.   4 drops per 100 ml. solution.

pH = 1.4   pH = 2.0
   pink   yellow

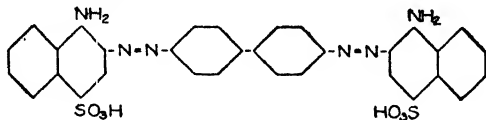*Thymol Blue.   Thymol-sulfon-phthalein (Clark and Lubs).*

Mol. wt. 466

0.040 g. in 100 ml. 95% alcohol = 0.0008 *M*.   2–4 drops per 100 ml. solu-
   tion.

pH = 2.0   pH = 2.4   pH = 2.8   pH = 8.4   pH = 9.2
   pink   salmon   yellow   gray green   blue

*Congo Red, Schultz No. 307. Diphenyl-disazo-bis-α-naphthyl-amine-4-sulfonic Acid.*

Mol. wt. 652

0.050 g. in 100 ml. 70% alcohol = 0.0008 *M*.   3–4 drops per 100 ml. solution.

pH = 3.3   pH = 3.9   pH = 4.6
blue   violet   pink

This indicator gives a satisfactory end point in going from blue to pink, but not the other way.   It is used in the Kjeldahl determination of ammonia.

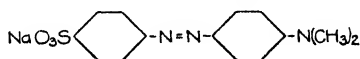*Brom-Phenol Blue.   Tetra-bromo-phenol-sulfon-phthalein (Clark and Lubs).*
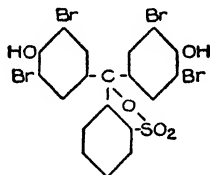
Mol. wt. 856

0.040 g. in 100 ml. 95% alcohol = 0.0005 *M*.   3–6 drops per 100 ml. solution.

pH = 3.2   pH = 4.0
yellow   violet

Methyl Orange, Helianthin, or Tropaeolin D; the Sodium Salt of Dimethylamino-azo-benzene-sulfonic Acid, Schultz No. 138.


Mol. wt. 327

0.020 g. in 100 ml. water = 0.0006 *M*.   2–4 drops per 100 ml. solution.

pH = 4.4   pH = 4.6
pink   yellow

The color change is very sharp provided that too much indicator is not employed.   Methyl orange is much used in the standardization of hydrochloric and sulfuric acids against sodium carbonate.   For such titrations the average deviation should not be greater than 1 part per 1,000, while with care a deviation of 1 part per 2,500 may be obtained.

Methyl Red, Schultz No. 138.   o-Carboxy Benzene-azo-dimethyl-aniline (Clark and Lubs).   Discovered by Rupp and Loose, *Ber.* 41, 3905 (1908).


Mol. wt. 269
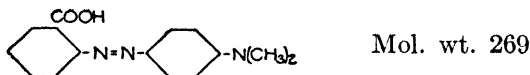
0.100 g. in 100 ml. 95% alcohol = 0.004 *M*.   2–4 drops per 100 ml. solution.

pH = 4.8   pH = 5.4
  pink   yellow

Different samples of this indicator seem to give different results as regards the sharpness of the color change.   While a great deal has been claimed for this indicator, the authors were unable to get as satisfactory results with it as with methyl orange.

Lacmoid or Resorcin Blue, Schultz No. 648.   Ammonium Salt of Tetra-bromo-hydroxy-diphenoxazone.

Mol. wt. 546
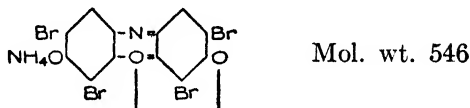
0.020 g. in 100 ml. of 50% alcohol (by warming to 50°) = 0.0004 *M*.   2–4 drops per 100 ml. solution.

pH = 4.4   pH = 5.2   pH = 6.2
  pink   violet   blue violet

*Cochineal, Schultz No. 932.*

Cochineal is the female of the *Coccus cacti*, an insect found growing on certain varieties of the cactus plant in Mexico and Central America.   A solution of cochineal is prepared for indicator purposes in accordance with the directions given by the *A. O. A. C. Bulletin*, **107,** p. 6 (1912), as follows: 3 g. of pulverized cochineal are digested with frequent agitation in a mixture of 50 ml. of strong alcohol and 200 ml. of distilled water for a day or two at ordinary temperatures.   The solution is then filtered and is ready for use.   The active color principle of this solution is carminic acid, for the formula of which see below.

2–4 drops per 100 ml. solution.

pH = 4.8   pH = 5.5   pH = 6.2
  yellow   pink   violet

Carminic Acid.

Carminic acid is the color principle of cochineal from which it can be prepared by the method of Schutzenberger as described in Allen's "Commercial Organic Analysis," Vol. **3**, Part 1, p. 464 (1900). The constitution of carminic acid, while not yet fully elucidated, is probably very close to the following:

Mol. wt. 478
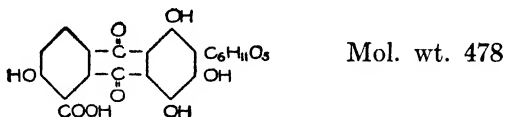
0.100 g. in 100 ml. water = 0.002 M.   2–4 drops per 100 ml. solution.

pH = 4.8   pH = 5.5   pH = 6.2
  yellow   pink   violet

Litmus or Tournesol.

Litmus or Tournesol is the substance resulting from the fermentation of various species of Rocella, Variolaria, and Lecanoria in the presence of small amounts of potassium carbonate. The fermented liquid is mixed with chalk or gypsum and made up into small cubes, in which form it comes into commerce. The coloring matter is a mixture of several substances, chiefly a red coloring-matter and a blue coloring-matter, the latter consisting mostly of azolitmin. The presence of the red coloring-matter is objectionable because it gives a red color which is not affected by a change in the hydrogen ion concentration of the solution, and hence tends to mask the color change of the azolitmin. In order to get rid of the red coloring-matter, the cubes should be extracted several times with alcohol. The residue is then extracted several times with water, the first portion being discarded because it contains the bulk of the potassium carbonate. The remainder of the water extract is acidified with dilute sulfuric acid and boiled for some time to expel carbonic acid. The excess of sulfuric acid is then carefully neutralized with barium hydroxide solution, and the barium sulfate filtered off.

On account of the variability of the amount of azolitmin in the resulting litmus solution, it is not possible to say how many drops of indicator to use; the analyst must use his own judgment.

pH = 5.0   pH = 5.5   pH = 6.0
 red   violet   blue

The use of litmus, or of azolitmin for that matter, for titration purposes is to be condemned. It should serve only for making rough qualitative tests, and then the litmus paper is to be preferred to the solution.

Azolitmin.

Azolitmin is the characteristic coloring-matter of litmus. It is prepared by slightly acidulating a solution of litmus, obtained as directed under the remarks concerning litmus, with hydrochloric acid. This gives on heating a precipitate which, after being washed and dried, is regarded as pure azolitmin.

0.050 g. in 100 ml. water.   2–4 drops per 100 ml. solution.

pH = 5.0   pH = 5.5   pH = 6.0
   red   violet   blue

p-Nitro Phenol.
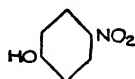
Mol. wt. 123

0.050 g. in 100 ml. 50% alcohol = 0.004 M.   2–5 drops per 100 ml. solution.

pH = 5.0   pH = 5.8
  colorless   faint yellow green

Brom-Cresol Purple. Di-bromo-o-cresol-sulfon-phthalein (Clark and Lubs).
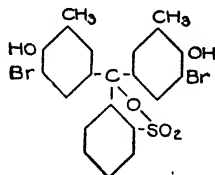
Mol. wt. 540

0.040 g. in 100 ml. 95% alcohol = 0.0008 M.   2–4 drops per 100 ml. solution.

pH = 5.8   pH = 6.2
  drab   purple

Neutral Red, Schultz No. 670.
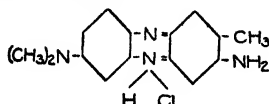

Mol. wt. 288

0.020 g. in 100 ml. 50% alcohol = 0.0007 M.   2–4 drops per 100 ml. solution.

pH = 5.4   pH = 6.0
  pink   colorless

Rosolic Acid, Aurin, Schultz No. 555.
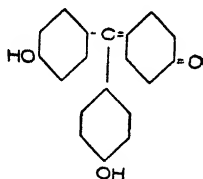
Mol. wt. 290

0.080 g. in 100 ml. 50% alcohol = 0.003 *M*.   2–4 drops per 100 ml. solution.

pH = 6.4   pH = 6.8
 yellow   pink

Brom-Thymol Blue.   Di-bromo-thymol-sulfon-phthalein   (Clark and Lubs).
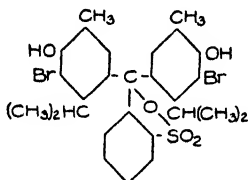
Mol. wt. 624

0.040 g. in 100 ml. 95% alcohol = 0.0006 *M*.   2–4 drops per 100 ml. solution.

pH = 6.4   pH = 7.0
yellow green   green

Phenol Red.   Phenol-sulfon-phthalein (Clark and Lubs).

Mol. wt. 354

0.020 g. per 100 ml. of 95% alcohol = 0.0006 *M*.   3–6 drops per 100 ml. solution.

pH = 7.0   pH = 7.4
 yellow   red

Cresol Red.　o-Cresol-sulfon-phthalein (Clark and Lubs).
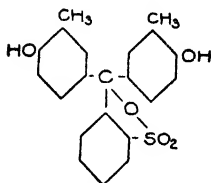
Mol. wt. 382

0.040 g. per 100 ml. of 95% alcohol = 0.001 *M.*　2–4 drops per 100 ml. solution.

pH = 7.6　　　pH = 8.2
　yellow　　　　　lilac

Phenolphthalein.
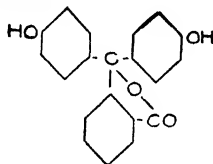
Mol. wt. 318

0.050 g. in 100 ml. of 50% alcohol = 0.0016 *M.*　2–4 drops per 100 ml. solution.
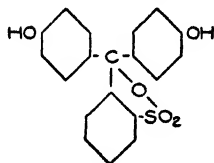
pH = 7.8　　　pH = 8.0
　colorless　　　　pink

Phenolphthalein cannot be used as an indicator if an acid solution containing an ammonium salt is being titrated by means of a base, because the repression of the hydroxyl ion by the ammonium ion necessitates that more alkali will have to be added to establish the end point than corresponds to the stoichiometric point.

Tropaeolin 000, Orange I, Schultz No. 144.　Sodium salt of p-sulfobenzene-azo-α-naphthol.
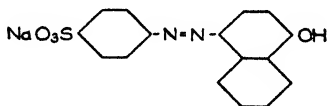
Mol. wt. 350

0.040 g. in 100 ml. of 95% alcohol = 0.001 *M.*　2–4 drops per 100 ml. solution.

pH = 7.6　　　pH = 8.9
　orange　　　　scarlet

[201]

Thymol Blue (Clark and Lubs).

pH = 8.4   pH = 9.2   This indicator has been described earlier
gray green   blue   in the paragraph, for pH = 2.0.

Thymolphthalein.
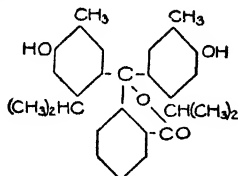
Mol. wt. 430

0.080 g. in 100 ml. 50% alcohol = 0.002 *M*.   2–4 drops per 100 ml. solu-
    tion.

pH = 7.9   pH = 8.9
colorless   blue

Cresolphthalein.   o-Cresolphthalein (Clark and Lubs).
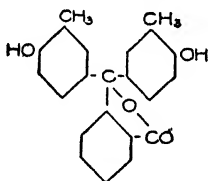
Mol. wt. 346

0.020 g. in 100 ml. of 95% alcohol = 0.0006 *M*.   2–4 drops per 100 ml.
    solution.

pH = 8.2   pH = 9.2
colorless   red

Alizarine Yellow G. m-Nitrobenzene-azo-salicylic Acid.

Mol. wt. 287

0.030 g. per 100 ml. of 95% alcohol = 0.001 *M*.   2–4 drops per 100 mL.
    solution.

pH = 10.1   pH = 12.1
colorless   yellow

Tropaeolin 0, Chrysoin, or Resorcin Yellow.   Resorcin-azo-p-benzene-sulfonic-acid.

$$HO_3S\langle\;\rangle-N\text{·}N-\langle\;\rangle-OH \qquad \text{Mol. wt. 316}$$
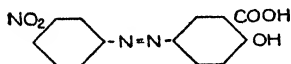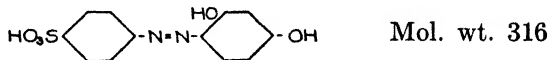
0.030 g. per 100 ml. of 95% alcohol = 0.001 M.   2–4 drops per 100 ml.
   solution.

pH = 11.1   pH = 12.7
   yellow   orange

154. Examples.

1. In performing the titration of hydrochloric acid with sodium hydroxide shown in Figure 33, what error, in parts per 1,000 would have resulted from the use of those indicators listed below which are described in § 153?

   (*a*) Tropaeolin OO, Orange IV, Shultz No. 139
   (*b*) Alizarine Yellow G
   (*c*) Cresolphthalein

2. In performing the titration of acetic acid with sodium hydroxide shown in Figure 34, what error in parts per 1,000 would have resulted from the use of those indicators listed below which are described in § 153?

   (*a*) Brom-Phenol Blue
   (*b*) Methyl Red, Shultz No. 138
   (*c*) p-Nitro Phenol
   (*d*) Neutral Red, Shultz No. 670

3. List those indicators described in § 153 which, as far as the pH range within which the color change takes place is concerned, would be suitable for the titration of acetic acid with sodium hydroxide solution of Figure 34.

4. What is the approximate hydrogen ion concentration of a solution of acetic acid having a pH of 3.5?

5. What is the approximate pH of a solution having a hydroxyl ion concentration of 4.2×10^{-5}?

6. What is the approximate pH of 0.1 M NH$_4$OH solution?

7. A solution of acetic acid having a volume of 175 ml. is titrated with 25.00 ml. of 0.1022 M NaOH solution at 25°.   Calculate the approximate pH at the beginning of the titration and at the stoichiometric point.

8. Calculate the per cent of hydrolysis of 0.01 M sodium formate at 25°.

9. Compare the concentration of sulfide ion in a 0.1 M solution of sodium sulfide with that in a 0.1 M solution of ammonium sulfide.

10. Plot the approximate curve for the titration of a solution of formic acid having a volume of 100 ml. with 30.00 ml. of 0.0801 M NaOH solution.

11. Plot the approximate curve for the titration of 125 ml. of NaOH with 20.50 ml. of 0.1120 M HCl.

12. State·briefly the meaning of each of the following: stoichiometric point, point of inflection, end point.

13. In preparation of a new acid, 2 : 5 Diamino-l-methyl-benzene-4 thiosulfuric acid, $C_7H_{10}N_2O_3S_2$, 0.1000 g. of the acid was dissolved in 100 ml. of water and titrated potentiometrically with 0.0202 M NaOH at 25°. The pH's so determined were:

ml. NaOH Added	pH	ml. NaOH Added	pH
0.00	4.16	20.00	7.25
0.95	4.42	20.50	7.66
2.50	4.73	20.75	8.19
5.00	5.10	21.10	8.71
7.50	5.36	21.50	9.27
9.00	5.49	22.00	9.58
10.00	5.58	23.00	9.99
12.00	5.75	24.00	10.27
14.00	5.94	26.00	10.55
16.00	6.17	28.00	10.74
19.00	6.74	30.00	10.84
19.50	6.93	32.00	10.92

— M. G. Sevag, Dissertation
Columbia University, 1929.

Plot the results and determine the point of inflection. Calculate the stoichiometric point, and ascertain the basicity of the acid.

14. Calculate the corresponding pH for each concentration of hydrogen ion calculated in Examples 1, 3, 4, 5, 6 and 7 of § 129.

· 15. What will be the colors of the indicators considered in this chapter when added to solutions which are (a) 0.1 molar with respect to $HC_2H_3O_2$, (b) 0.1 molar with respect to both $HC_2H_3O_2$ and $NaC_2H_3O_2$, (c) 0.1 molar with respect to $NaC_2H_3O_2$, (d) 0.1 molar with respect to NH_3?

CHAPTER VIII

STANDARD ACIDS AND ALKALIES

155. Standard Solutions. — In the actual application of aci-dimetry-alkalimetry it is necessary to employ standard solutions of acids and alkalies, namely, those whose concentrations are definitely known. A standard solution can be prepared in two ways:

1. It can be made up carefully to the desired concentration.

2. It can be made up to approximately the desired concentration and its exact value determined by standardization.

When a solute having a definite composition can be measured out with precision and also when the dissolving of the solute does not change the effectiveness of the solute, then the first method can be employed by simply dissolving a definite quantity of solute and diluting to a definite volume. In a great many cases these requirements cannot be satisfied, so that in order to make up a solution of definite concentration it is necessary to make up the solution to a greater strength than is required, then to determine its value, and to dilute accordingly to bring its value down to the exact figure desired, and finally to determine its new value. As this procedure involves two standardizations with an intervening dilution, the second method has come into vogue, that is, of making up the solution to approximate concentration, determining its value exactly and then using it as it is.

156. Methods of Expressing Concentration. — The value of a standard solution can be expressed in terms of

1. Normality,

2. Molarity,

3. Weight of constituent being determined,

4. Per cent of constituent being determined.

It is advisable to consider these systems briefly together with their inherent advantages and disadvantages.

157. *Normal Solutions*. — The scheme of normality[1] is based on the use of the gram equivalent weight as the unit weight of reagent to be employed in making up standard solutions, namely, that weight of reagent which corresponds to or brings into reaction one gram equivalent of an element, or, more specifically, that weight which corresponds to or brings into reaction 1.008 g. of hydrogen or 126.9 g. of iodine. The number of gram equivalents of reagent per liter of solution is the normality of a solution. Thus, one gram equivalent of reagent per liter of solution constitutes a normal solution; one-tenth of a gram equivalent per liter of solution, a tenth normal solution, etc. The capital letter N is used as an abbreviation for normal. The idea back of this scheme is that if solutions are made up to contain the same number of gram-equivalents of reagents per equal volumes, then for many of these solutions, though not for all, 1 ml. of one solution will furnish just the amount of reagent demanded by 1 ml. of the other.

The great disadvantage of this scheme is the ambiguity to which it often leads because of the fact that the weight of reagent necessary to make a normal solution depends upon the purpose for which it is used.[2] In the case of phosphoric acid, reactions

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[1] According to A. Classen, "Friedrich Mohr's Lehrbuch der Chemisch-Analytischen Titrirmethode," 7th ed., p. 56, Fr. Vieweg u. Sohn, Braunschweig, 1896.

So far as is known, this scheme was first introduced by John Joseph Griffin of London about 1860 in the effort to bring about a uniformity in the employment of standard solutions which before that time had been used without reference to any special system. It was adopted by Mohr and largely extended by Mohr during the period.

[2] F. P. Treadwell, "Analytical Chemistry," translation by W. T. Hall, Vol. II, "Quantitative Analysis," 8th ed., p. 473, John Wiley and Sons, Inc., New York, 1935.

G. Lunge, "Technical Methods of Chemical Analysis," translation by C. A. Keane, Vol. I, Part I, p. 45, Gurney and Jackson, London, 1924. Lunge claims that in figuring the weight of reagent corresponding to 1.008 g. of hydrogen, it should be figured in terms of the substance to be examined and says that it is only accidental when the ratio of the gram equivalents refers to the composition of the normal solution itself.   On this basis a normal solution of phosphoric acid would contain 98.14 g. H_3PO_4 if figured in terms of the sodium hydroxide required for titration with methyl orange as indicator, or 49.07 g. H_3PO_4 if phenolphthalein were used as indicator.

proceeding to each of the three stoichiometric points and the corresponding equivalent weights are

$$H_3PO_4 + OH^- \rightarrow H_2O + H_2PO_4^- \qquad \frac{98.09}{1} = 98.09 \text{ g.}$$

$$H_3PO_4 + 2OH^- \rightarrow 2H_2O + HPO_4^= \qquad \frac{98.09}{2} = 49.05 \text{ g.}$$

$$H_3PO_4 + 3OH^- \rightarrow 3H_2O + PO_4^\equiv \qquad \frac{98.09}{3} = 32.70 \text{ g.}$$
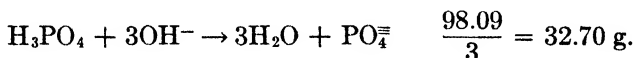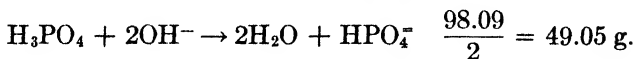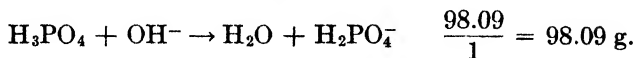
In a similar manner, the weights of $KMnO_4$ required for a liter of normal solution depends on the type of change it undergoes. For the changes represented below, the corresponding equivalent weights would be used

$$5e + 8H^+ + MnO_4^- \rightarrow Mn^{++} + 4H_2O \qquad \frac{158.03}{5} = 31.61 \text{ g.}$$

$$3e + 4H^+ + MnO_4^- \rightarrow MnO_2 \downarrow + 2H_2O \qquad \frac{158.03}{3} = 52.68 \text{ g.}$$
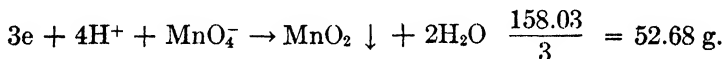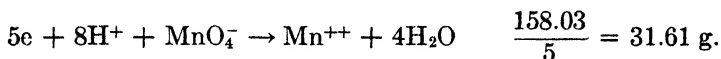
In these cases and in many others it would be open to doubt as to what is meant by a normal solution unless some explanatory note were given in the text. The scheme of normality as a basis of definition is inadequate and should be abandoned.

158. Molar Solutions. — The scheme of molarity is based on the use of the mole as the unit weight of reagent to be employed in defining standard solutions, namely, that weight of reagent which represents the molecular or formula weight in grams.[3] The number of moles of reagent per liter of solution is the molarity of a solution. Thus, one mole per liter of solution constitutes a molar solution; one-tenth of a mole per liter of solution, a tenth molar solution, etc. The capital letter M is used as an abbreviation for molar. The great advantage of this scheme is its freedom from all ambiguity and the ease which it contributes in the handling of analytical data, particularly data relating to oxidation-reduction reactions.

[3] The use of the term *mole* was proposed and introduced by Ostwald. It is of very great importance in that it brings out very clearly many fundamental chemical relationships which otherwise would be scarcely discernible. In this regard see any textbook on physical chemistry.

As examples of molar solutions, a molar solution of hydrochloric acid contains 36.47 g. HCl, of sulfuric acid 98.09 g. H_2SO_4, of oxalic acid 126.05 g. $H_2C_2O_4 \cdot 2H_2O$, of potassium dichromate 294.20 g. $K_2Cr_2O_7$, all per liter of solution.

' **159. Value of Solution in Terms of Weight of Constituent being Determined.** — A scheme which is often used in routine work expresses the value[4] of a standard solution in terms of the constituent which is to be determined. This scheme is convenient in that the weight of the constituent is found at once by multiplying the number of milliliters of standard solution used by the value of one milliliter.

By way of illustration, let us suppose that 1.00 ml. of HCl has been found to be equivalent to 0.005442 g. of Na_2CO_3 when methyl orange is used as the indicator.   If 30.00 ml. of this same solution is used in titrating an unknown quantity of Na_2CO_3 using the same indicator, obviously the weight of Na_2CO_3 in the sample is

$$30.00 \times 0.005422 = 0.1627 \text{ g. } Na_2CO_3.$$

If 45.00 ml. of this same solution is used to titrate K_2CO_3, we can calculate the weight of K_2CO_3 titrated from the Na_2CO_3 value of the solution and the chemical factor

$$\frac{K_2CO_3}{Na_2CO_3} = \frac{138.20}{106.00} = 1.3038$$

$$45.00 \times 0.005422 \times 1.3038 = 0.3181 \text{ g. } K_2CO_3.$$

160. Value of Solution in Terms of Per Cent of Constituent being Determined. — The practice of making up standard solutions to an arbitrary factor value, when the factor value is so selected that the burette readings of the standard solution will give directly the percentage of the unknown constituent which is being titrated, is particularly suited to routine work. We will now show how the selection of such a factor value is arrived at.

[4] By the *value of a solution* we shall mean any measure which either directly or indirectly gives the weight of reagent which the solution contains per unit volume.

Let p = % constituent to be represented by 1 ml. of standard solution;

  f = value of the standard solution in terms of the constituent being determined, *i.e.*, the number of grams of constituent corresponding to 1 ml. of the standard solution;

  n = number of ml. of standard solution used in the titration;

  W = the weight of sample taken for analysis.

Then, $\dfrac{nf}{W} \times 100$ = % constituent in sample,

also np =   "   "   "   "

whence, by equating, we get

$$f = \frac{pW}{100}.$$

It is evident from the foregoing relationship that if we arbitrarily fix the value of p, we can vary f and W; if, however, p and W are fixed, there is only one value of f that will satisfy the equation.

By way of illustration, let us suppose that it is required to make up a standard hydrochloric acid solution of such a value that 1 ml. of it shall correspond to 2% sodium carbonate, when 1 g. of the sample containing the sodium carbonate is taken for analysis, and methyl orange is used as the indicator in the titration. We have

$$f = \frac{2 \times 1}{100} = 0.0200;$$

namely, 1 ml. of the hydrochloric acid solution shall be equivalent, to 0.0200 g. Na_2CO_3, or from the reaction:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$
$$106.00 \qquad 2(36.47)$$
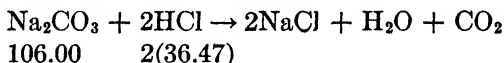
1 ml. of the standard solution shall contain 0.01376 g. HCl.

The plan of adjusting the weight of the sample to the strength of the solution is particularly advantageous in routine work where use is made of a standard solution which changes in strength and has to be frequently restandardized. In any case, however, where this system is to be used, it is necessary that the sample which is to be weighed out be in a finely pulverized condition;

with a coarsely divided substance, like iron drillings for instance, one might easily lose more time in adjusting the exact weight of material on the balance pan than would be saved in the calculation.

161. *Value of Solution in Terms of Weight of Solute.* — The scheme of expressing the value of a standard solution in terms of the weight of dissolved reagent is not much used, because a great part of volumetric analysis consists in the routine determination of some given constituent which is different from the dissolved reagent, and therefore this would necessitate for each titration, in order to arrive at the weight of the constituent sought, an intermediate calculation of the weight of standard reagent corresponding to the volume of standard solution used — a roundabout procedure which can almost always be abridged by employing some one of the other schemes.

In conclusion, as to the various ways of expressing the values of standard solutions it should be pointed out that, while it is a matter of choice as to which scheme shall be employed, it is usual to select that one which will lend itself most readily to a simplification of the subsequent calculations.

162. Standard Acids. — There are practically only two acids which are suitable for general use as acidimetric standards, namely, hydrochloric and sulfuric. Nitric acid, although it is likewise a strong acid, is not desirable because it almost invariably contains a small percentage of nitrous acid which has a destructive action on the two important indicators, methyl orange and methyl red.

The primary standard that is used volumetrically to standardize either hydrochloric [5] or sulfuric acid [6] is sodium carbonate in

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[5] Hydrochloric acid is also standardized gravimetrically by the following methods: (a) by precipitation as silver chloride, see § 204; (b) by neutralization with ammonium hydroxide, evaporation to dryness of the ammonium chloride and determination of the ammonium chloride by loss of weight upon volatilization. The first method, although it is the one used for atomic weight determinations, does not give good results in the hands of students, the results being from 5 to 20 parts per 1,000 low. The second method requires the use of large platinum dishes (of about 80 to 100 ml. capacity) so that its general use is largely restricted.

[6] Sulfuric acid is also standardized gravimetrically by precipitation as barium sulfate.

conjunction with either methyl orange or methyl red as indicator. The sodium carbonate must be prepared as described herewith.

163. Preparation of the Sodium Carbonate. — About 5 g. of pure sodium bicarbonate is placed in a platinum or a glazed porcelain crucible, and the crucible with its contents is then put on a sand bath;[7] the sand is piled about halfway up the sides of the crucible. A 360° thermometer is inserted in the bicarbonate and the sand bath so heated that the thermometer registers a temperature between 270° and 300° for an hour. At this temperature the bicarbonate is converted to the carbonate according to the reaction

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

The heating must be watched carefully, as frequently the temperature begins to mount very rapidly and will go beyond 300° unless checked, and at temperatures much above 300° we have enough decomposition of the carbonate into oxide according to the reaction.

$$Na_2CO_3 \rightarrow Na_2O + CO_2$$

to vitiate its use as a standard for purposes of titration.[8] The carbonate is cooled in a desiccator for 30 minutes and weighed. The heating is repeated for half-hour periods until constant weight is obtained, when the carbonate is ready for use. It is kept in its containing crucible in the desiccator and, as needed, small portions are withdrawn by means of a spatula.

If a supply of pure sodium bicarbonate is not at hand, a good grade of "Analyzed" sodium carbonate may be used in its place.

164. Preparation and Standardization of Approximately 0.1 M Hydrochloric Acid by Means of Sodium Carbonate. — In preparing the acid, about 600 — 700 ml. of distilled water is poured

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[7] Instead of a sand bath, an air bath may be used. A most excellent and simple air bath is made by taking a silica beaker about 6.5 cm. diameter by 8 cm. high, fitting it about 1 cm. from its top with a wire triangle made of some difficultly oxidizable wire (preferably manganin), so arranging the construction that the sides of the triangle extend a suitable length to engage a 9 cm. iron ring by means of which the beaker is suspended from a ring stand. Inside of the beaker, for the purpose of supporting the crucible to be heated, is placed a small triangle with its legs bent at right angles and cut to such length that the plane of the triangle shall be about 2 cm. above the floor of the silica beaker.

[8] W. C. Ferguson, *J. Soc. Chem. Ind.* (London), **24**, 781 (1905).

into a clean liter flask and then 8.5 ml. of concentrated (12 M) hydrochloric acid [9] is added. The solution is made up to the mark with water and mixed thoroughly by shaking. This will give a solution which is approximately 0.1 M. The solution is transferred to a clean, two-liter, glass-stoppered bottle.[10]

In the standardization of the acid, three beakers, of about 300 ml. capacity each, are selected as nearly alike in form and color as is practicable.[11] The sodium carbonate is weighed out upon a tared watch-glass, or from a weighing bottle, in successive portions of about 0.160 g., 0.175 g., and 0.190 g., to the nearest tenth of a milligram. If a tared watch-glass is used, the samples are transferred to the several beakers by means of a camel's-hair brush. In handling the watch-glass upon which the sodium carbonate is placed, the watch-glass should not be touched by the fingers but by means of tongs, because the fingers, even though freshly cleaned, will leave enough perspiration or grease to cause an error of several tenths of a milligram in the weighing.

After all the portions of sodium carbonate have been weighed out, 125 ml. of water and 2 − 4 drops of methyl orange solution are added to each beaker. A 50 ml. burette is filled to the zero mark with the acid to be standardized. The beaker containing the lightest sample is placed upon an unglazed piece of white paper [12] under the burette and, while stirring the solution in the beaker, the acid is run in slowly from the burette, until the color of the methyl orange becomes a very faint yellow. The walls of the beaker are then washed down with distilled water and the titration is very carefully resumed by adding the acid, a drop at a time, until the color of the methyl orange becomes a faint pink. This marks the end point of the titration. The burette reading is noted after waiting the customary 30 seconds for drainage.

[9] Concentrated hydrochloric acid, sp. gr. 1.19, 36–37%, as generally supplied is usually about 12 M. The constant boiling point hydrochloric acid, *i.e.*, that which boils at 110° under 760 mm. pressure, is about 6.1 M. See § 165.

[10] The two-quart bottles in which acids are usually supplied for the laboratory serve excellently for this purpose.

[11] Pyrex glass. owing to its greenish yellow tint, is not desirable for use in the present titration.

[12] A 12½ cm. filter paper answers admirably for this purpose.

If the first sample titrated is the lightest and requires, say, 30.20 ml., then the next heavier sample will require somewhat more than 30.20 ml. Its titration can be performed rapidly to within 2.00 ml. of the estimated end point after which the acid is added more slowly until the end point is reached. This will often result in the saving of much time. At no time should the acid be run out of the burette in a steady stream. In estimating the volumes of acid for the second and third titrations, ample allowance must be made for an error in the previous titration. If this is not done there is danger of going beyond the end point in these titrations.

There is often difficulty in judging the color change of methyl orange because of the fact that too much of this indicator has been employed. Methyl orange is peculiar in that it gives the sharpest color change when the amount of it that is used is the *least* amount that is plainly noticeable; if too much of it is used, the color change becomes indefinite owing to the development of an intermediate claret-brown tint during the color transition.

The contents of the other two beakers are similarly titrated, titrating the heaviest sample last. From the weights of the sodium carbonate and the volumes of hydrochloric acid employed the number of grams of sodium carbonate equivalent to 1 ml. of the acid [13] is calculated to four significant figures for each titration. The average deviation of these three results should not be greater than one part per 1,000. If the average deviation is greater than this, further titrations must be run until the average deviation, excluding those results which are doubtful, in accordance with our criterion for the rejection of doubtful observations, is within one part per 1,000.[14] The arithmetical mean is then taken as the value of the solution.

The standardization data can be conveniently tabulated in the notebook and on the report card as shown in Table 30.

[13] Failure to correct for the amount of solution necessary to affect the indicator introduces a slight error which cancels out if the same volume of standard solution is used in the titration of an unknown as was used in the standardization.

[14] If this precision is not obtained after repeated trials the analyst should test himself for color blindness by the method of Ishihara, "Tests for Colour-Blindness," 7th ed., C. H. Stoelting Co., agents, Chicago, 1936.

Table 30

SUGGESTED FORM FOR STANDARDIZATION REPORT

	Standardization of HCl			
Name_____ ____			Date Begun_____	
Balance No._____			Date Finished_____	
Burette No._____				

No.	g. Sample	ml. HCl	g. Sample $\equiv$ 1 ml. HCl	Deviation Parts/1,000
1				
2				
3				
	Na$_2$CO$_3$ value		_____	_____a.d.

Indicator_____

Molarity_____   Signature_____

The Na$_2$CO$_3$ value of the HCl is the mean value for the number of grams of Na$_2$CO$_3$ equivalent to one milliliter of the solution. The molarity of the HCl can be calculated from the Na$_2$CO$_3$ value. By way of illustration let us suppose that when methyl orange was used as the indicator the value for the average of three determinations was found to be

$$1 \text{ ml. HCl} \equiv 0.005468 \text{ g. Na}_2\text{CO}_3.$$

At the stoichiometric point we have,
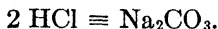
It follows that $$2 \text{ HCl} \equiv \text{Na}_2\text{CO}_3.$$

$$2{,}000 \text{ ml. of } M \text{ HCl} \equiv 106.00 \text{ g. Na}_2\text{CO}_3$$

and the Na$_2$CO$_3$ value of a molar solution is,

$$1 \text{ ml. of } M \text{ HCl} \equiv \frac{106.00}{2{,}000} = 0.05300 \text{ g.}$$

The Na$_2$CO$_3$ value of the HCl being standardized, divided by the Na$_2$CO$_3$ value of a molar solution, gives the molarity sought; or,

$$\frac{0.005468}{0.05300} = 0.1032 \, M.$$

165. Preparation of Standard Hydrochloric Acid from Constant Boiling Acid. — It has been shown [15] that at a definite pressure and at a definite rate of distillation the distillate from constant boiling HCl has a sufficiently definite composition to make possible its use in preparing standard solutions of HCl. Concentrated C.P. HCl is diluted to a specific gravity of 1.1 and distilled at the rate of 3 to 4 ml. per minute. The distillate is not collected until 75% of the liquid has distilled, and distillation is discontinued when about 6% of the original volume remains as a residue.

Table 31 gives the composition of distillate obtained at a variety of pressures when the above procedure is followed.

Table 31

COMPOSITION OF DISTILLATE FROM CONSTANT BOILING HYDROCHLORIC ACID

Pressure mm. Hg	HCl Vacuum Wt. Basis, %	Air Wt. of Distillate Containing 1 Mole Vacuum Wt. of HCl, g.
770	20.197	180.407
760	20.221	180.193
750	20.245	179.979
740	20.269	179.766
730	20.293	179.555
700	20.351	179.008
660	20.438	178.244
650	20.471	177.967
640	20.504	177.671

After preparing the constant boiling HCl and noting the barometric pressure at the time of distillation, the approximate amount of acid needed for one liter of 0.1 M HCl is weighed out, in a small glass-stoppered flask, to the nearest milligram. The contents of the flask are then carefully transferred to a liter flask and diluted to the mark with distilled water. The molarity of the acid is then calculated as follows:

$$\frac{\text{weight of acid}}{\text{weight of acid needed for 1 liter of molar solution}} = \text{Molarity.}$$

[15] Faulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923); Bonner and Branting, *ibid.*, **48**, 3093 (1926).

By way of illustration, let us suppose that 17.9986 g. of acid prepared at a pressure of 740 mm. was used in making one liter of solution. The molarity of the solution would be

$$\frac{17.9986}{179.766} = 0.10012 \, M.$$

166. Labeling Standard Solutions. — Immediately upon obtaining the value of any solution, the analyst should paste upon the stock bottle containing the solution a label bearing the name of the reagent, the value of the solution, the date of standardization and the initials of the person making the standardization, thus:

Hydrochloric Acid
0.1098 M
8.12.38   H. A. F.

167. Cautions about the Use of Standard Solutions. — Before withdrawing any standard solution from its stock bottle, the chemist should always do two things: first, he should shake the stock bottle vigorously because very often some water distills from the solution and collects upon the inner upper walls of the bottle, thereby changing the value of the solution unless remixed with it; second, he should wipe the mouth of the bottle carefully with a damp cloth to remove any dirt or foreign matter that might have collected.

Having once withdrawn some standard solution from its stock bottle, any unused portion of it should never be returned to the bottle, as such practice is extremely threatening to the reliability of the solution.

168. Standard Alkalies. — It is to be observed that all alkaline solutions are subject to deterioration upon standing because of the absorption of carbon dioxide from the air and the action of alkaline solutions on the glass of the containing vessels. Therefore it becomes necessary to redetermine or check the value of all alkaline solutions practically every day that they are used. From what has been said under the theory of acidimetry-alkalimetry, § 146,

it follows that a strong base is the only one that is suitable for the general purposes of titration.   There are three strong bases available, namely, potassium hydroxide, sodium hydroxide, and barium hydroxide; of these sodium hydroxide is more generally used because it can be more easily secured on the market.   Even the best grades of this chemical, however, contain small amounts of chlorides, sulfates, silica and alumina, besides more or less sodium carbonate and water, so that it is advisable to weigh out about 10% more than the calculated amount when using it for the preparation of a standard solution.

169. Preparation of Sodium Hydroxide Solution. — To prepare the NaOH solution about 600–700 ml. of distilled water is poured into a clean liter flask after which 4.5 g. of stick sodium hydroxide is added, care being taken that the hydroxide is free from any visible encrusted carbonate.   The solution is made up to the mark with water and is thoroughly mixed by shaking, after which it is transferred to a clean stock bottle.

If a solution of sodium hydroxide, quantitatively free from carbonate, is desired, the sodium hydroxide solution is first made up in a bottle of suitable size, and enough barium hydroxide (or barium chloride) solution is added to precipitate the carbonate.

Fig. 44

Stock Bottle

The precipitate is allowed to settle overnight or so, and the clear solution is then siphoned off into another bottle which has a two-hole rubber stopper, one hole to accommodate a guard tube filled with soda lime, the other hole to accommodate the long
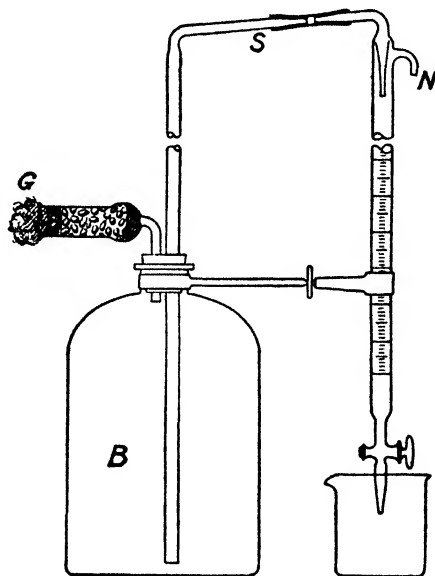
arm of the siphon used for conveying the solution from the stock bottle to a burette after the manner represented in Figure 44. The end of the siphon should be about one inch away from the bottom of the stock bottle so that the solution may be withdrawn without disturbing any slight precipitate of barium carbonate that may have formed. The burette is filled by applying suction at N. It is advisable to have the guard tube G bent at right angles, as enough moisture is sometimes absorbed to cause the soda lime to dissolve and if the tube were not at right angles the concentrated alkaline solution would drip into the stock bottle.

In many determinations the presence of a small amount of carbonate in the sodium hydroxide still allows a precision sufficient for the work in hand. When such is the case it is not necessary to go to the precautions described above, but only necessary to dissolve a good grade of sodium hydroxide and make up to volume forthwith. To assure himself of the amount of carbonate which may be present in the solution, the analyst should not merely accept the published figures giving the manufacturers' analysis of the sodium hydroxide but should run a differential titration using phenolphthalein and methyl orange (or methyl red) as indicators.

170. Standardization of Sodium Hydroxide by Means of Potassium Acid Phthalate. — Potassium acid phthalate, $C_6H_4(COOK)$-$COOH$, is a stable nonhygroscopic crystalline substance which dissolves readily in water. When obtained in the purified form it makes a very good standard for NaOH solution. In order to standardize this solution three samples of the potassium acid phthalate weighing between 0.600 and 0.800 g. are placed in 250 ml. beakers and dissolved in 125 ml. of distilled water. When these solutions are titrated with 0.1 M NaOH using phenolphthalein or thymol blue as the indicator the end point observed indicates that

$$NaOH \equiv C_6H_4(COOK)COOH.$$
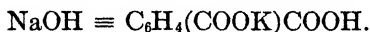
From this relationship and the weights of the samples and volumes of NaOH solution added, the molarity of the NaOH solution can be calculated. The data can be tabulated in a manner similar to that suggested in § 164 for the standardization of HCl.

171. Standardization of Sodium Hydroxide by Means of Benzoic Acid.—A primary standard for the standardization of either sodium hydroxide or potassium hydroxide solutions is benzoic acid in conjunction with phenolphthalein as indicator. The benzoic acid should not contain more than 0.1% of chlorine as chlor-benzoic acid.[16] This material may be safely used as an acidimetric sample in work requiring an accuracy of not more than one part in 2,000, provided the following precautions are carefully observed:

1. The acid should be carefully fused before use in a glass or platinum vessel placed in an air bath. The temperature during fusion must not rise above 140°; it is best to keep it below 130° and to cease heating as soon as fusion is complete.

2. The acid should be dissolved in 95% alcohol (about 20 ml. for a one gram sample) and a blank test made upon the same volume of alcohol so that the necessary correction may be applied in the subsequent titration.

3. The titration must be made in the cold with carbonate-free alkali and the necessary precautions taken to prevent the access of carbon dioxide from the air during the titration. Phenolphthalein is the most satisfactory indicator.

4. In the calculation of results, the acid value of the sample is to be taken as 0.9990 that of pure benzoic acid.

In this titration 25.00 ml. of a 0.1 M solution of NaOH is equivalent to 0.3051 g. C_6H_5COOH.

In using alcohol to dissolve the benzoic acid, it is preferable, though not absolutely necessary, to use alcohol which has been redistilled from potassium hydroxide, because such treatment of the alcohol eliminates small amounts of nitrogenous and acid principles ordinarily present in alcohol, thereby reducing the size of the blank. It will be found that some of the alcohol will soon evaporate during the first part of the titration leaving a slight ring of benzoic acid around the walls of the titrating vessel. Therefore, it becomes necessary toward the end of the titration to wash down the walls of the titrating vessel carefully to make sure that the deposited benzoic acid is included in the titration.

[16] Benzoic acid of the requisite purity can be obtained from the National Bureau of Standards; their Standard Sample No. 48, Benzoic Acid, C_6H_5COOH 99.9%, Acidimetric Standard is satisfactory.

For full directions regarding the use of benzoic acid, see articles by George W. Morey, *J. Am. Chem. Soc.* **34,** 1027 (1912), and E. R. Weaver, *ibid.* **35,** 1309 (1913).

172. Procedure in Standardization of Approximately 0.1 Molar Sodium Hydroxide by Means of Benzoic Acid. — The analyst should select three beakers of about 300 ml. capacity each, and should then weigh out upon a tared watch-glass the benzoic acid in successive portions of about 0.300 g., 0.310 g., and 0.320 g. to the nearest tenth of a milligram and should transfer the several portions to the respective beakers, observing the precautions of handling the watch-glass as mentioned in § 164. After the several portions have been weighed out, 10 ml. of alcohol and 3–5 drops of phenolphthalein solution are added to each. A standard 50 ml. burette is now filled to the zero mark with the sodium hydroxide solution, and the titration of the benzoic acid portions is conducted with due observance of the precautions mentioned in § 171. The first faint pink is taken as the end point; a blank is run on the same volume of alcohol, and the correction applied accordingly. The average deviation of the three titrations should not be greater than 1 part per 1,000.

173. Standardization of Sodium Hydroxide by Means of Standard Acid. — Standard hydrochloric or sulfuric acids are also used for the purpose of standardizing alkaline solutions, but they can only be regarded as secondary standards, since by their use we are basing a standardization upon a solution which itself has been standardized.

If a good primary standard is not at hand, the sodium hydroxide solution may be standardized by means of standard acid as follows. Three 25 ml. portions of the standard acid, approximately 0.1 *M*, are pipetted into separate beakers by means of a standard pipette; about 100 ml. of distilled water and 3–5 drops of phenolphthalein are added to each beaker. The titration is then conducted by adding the sodium hydroxide solution from the burette until the end point is reached. The average deviation of the three titrations should not be greater than 2 parts per 1,000.

174. Exercise No. 3. — Prepare and standardize 1 liter of approximately 0.1 *M* hydrochloric acid.

175. Exercise No. 4. — Prepare and standardize 1 liter of approximately 0.1 M sodium hydroxide solution.

176. Exercise No. 5. — Determine the amount of hydrochloric acid in an unknown solution furnished by the instructor.

177. Exercise No. 6. — Determine the amount of sodium carbonate in an unknown sample furnished by the instructor.

The data obtained can be conveniently tabulated on the report card in the manner shown in Table 32.

Table 32

SUGGESTED FORM FOR UNKNOWN REPORT

	Sodium Carbonate Unknown				
Name_____			Date Begun_____		
Balance No._____			Date Finished_____		
Burette No._____					
No.	g. Sample	ml. HCl	g. Na$_2$CO$_3$ in Sample	% Na$_2$CO$_3$ on Dry Basis	Deviation Parts/1,000
1					
2					
3					
		Mean			a.d.
Indicator_____					
Na$_2$CO$_3$ value of HCl_____					
Molarity of HCl_____					
Per cent moisture_____					
			Signature_____		

To illustrate the calculation of results let us suppose that a 1.0022 g. sample, containing 2.51% moisture, required 22.50 ml. of HCl solution when methyl orange was used as the indicator, and that 1.00 ml. of the HCl solution was equivalent to 0.005468 g. of Na$_2$CO$_3$ when methyl orange was used.   We have then

$$\frac{0.005468 \times 22.50 \times 100}{1.0022\,(1.0000 - 0.0251)} = 12.62\% \text{ Na}_2\text{CO}_3 \text{ on dry basis.}$$

178. Examples.

1. One milliliter of HCl solution is found to be equivalent to 0.005420 g. of Na_2CO_3 when methyl orange is used as the indicator. Calculate the molarity of the solution.

2. A 1.2024 g. sample of a mixture of sodium carbondate and potassium nitrate containing 1.01% moisture was titrated with 40.22 ml. of 0.08922 M hydrochloric acid. Methyl orange was the indicator. Calculate the per cent of Na_2CO_3 in the sample on the dry basis.

3. In standardizing an approx. 0.1 M solution of hydrochloric acid by titration against sodium carbonate, using methyl orange as indicator, the following results were obtained:

   0.1317 g. Na_2CO_3 required 22.83 ml. HCl
      .1391   "   "   24.08   "
      .1389   "   "   24.06   "
      .1279   "   "   22.18   "

What was the molarity of the hydrochloric acid? What was the average deviation? Should any of the results be rejected?

                                  Ans.   0.1089 M.   1 part in 2,000.   No.

4. A 2.1020 g. sample of a mixture of potassium carbonate and sodium nitrate was titrated with 25.68 ml. of a solution of HCl. Methyl orange was used as the indicator. One milliliter of the HCl solution used is equivalent to 0.0108 g. of Na_2CO_3 when phenolphthalein is used as the indicator. Calculate the per cent of K_2O in the sample.

5. Explain the effect on the calculated normality of HCl solution, if the acid is standardized against Na_2CO_3 which was prepared from $NaHCO_3$,

      (a) when the $NaHCO_3$ was heated for too short a time at too low a temperature,
      (b) when the $NaHCO_3$ was heated for too long a time at too high a temperature.

6. How many ml. of a 0.1039 M HCl solution would be required to titrate 0.2905 g. K_2CO_3, using methyl orange as the indicator?

                                    Ans.   40.46 ml.

7. 0.2047 g. Na_2CO_3 required 34.45 ml. of a certain hydrochloric acid solution to neutralize it when methyl orange was used as indicator. 27.54 ml. of a sodium carbonate solution required 33.46 ml. of the same hydrochloric acid for neutralization with methyl orange as indicator. What is the molar strength of the sodium carbonate solution?

                                  Ans.   0.0681 M.

8. 30.00 ml. of an approximately 0.2 M HCl solution gave 0.8042 g. of AgCl.   32.00 ml. of this acid were found to neutralize 34.62 ml. of a sodium carbonate solution, using methyl orange as indicator.   Find the value of the sodium carbonate solution.   Ans.   0.0865 M.

9. 0.2560 g. of a mixture containing Na_2CO_3 and NaOH was titrated with 0.1 M HCl.   It took 24.3 ml., using phenolphthalein as indicator, and then 19.17 ml. more, using methyl orange as indicator.   How many g. each of NaOH and of Na_2CO_3 were present?
                          Ans.   0.0205 g. NaOH.   0.2032 g. Na_2CO_3.

10. 2.00 ml. (by burette) of a sample of "potash liquor" were diluted to about 300 ml.   Using phenolphthalein as the indicator, 22.99 ml. of 0.9523 M HCl was required, and upon adding methyl orange 0.52 ml. more of the HCl was required.   The density of the original solution was 1.444 at 20°.   What was the percentage by weight of the KOH and K_2CO_3?   Ans.   KOH = 41.58%. K_2CO_3 = 2.37%.

11. In order to render citric acid $(CO_2H \cdot CH_2)_2 \cdot C(OH) \cdot CO_2H + H_2O$ anhydrous, Sörensen[17] recommends heating the acid at 70° under 20–30 mm. pressure until constant weight is obtained.   In testing a lot of citric acid, which had been so treated, 0.4004 g. of sample was dissolved in water and titrated with barium hydroxide solution and found to require 25.82 ml., using phenolphthalein as indicator.   20.00 ml. of the barium hydroxide solution was the equivalent of 48.42 ml. of 0.1000 M HCl solution.   What percentage of anhydrous citric acid did the sample contain?   Ans.   99.95%.

12. Verify the fact that, when a weight of sample is taken which is one hundred times the value of 1 ml. of the standard solution expressed in grams of the constituent being determined, the burette readings in milliliters give percentages direct.

13. A sample of soda weighing 25.00 g. is dissolved in water and made up to 250.0 ml., and one-fifth of this solution is taken for titration.   What must be the normality of the standard acid (assuming the alkalinity to be due wholly to Na_2CO_3) in order that twice the number of milliliters of acid used shall indicate the percentage of Na_2CO_3 in the sample?   See G. McPhail Smith, reference given in § 11.   Ans.   1.887 N.

14. In the estimation of small quantities of free CO_2 in water, an excess of $Ba(OH)_2$ is added to precipitate the CO_2 as barium carbonate.   The excess of $Ba(OH)_2$ is then titrated with oxalic acid, using phenolphthalein as indicator.   How many milliliters of 0.4875 M oxalic acid must be diluted to 1 liter in order to give a solution, 1 ml. of which would correspond to 1 mg. CO_2 in the above method?   Ans.   46.62 ml.

[17] *Biochem. Z.* **21**, 171 (1909).

CHAPTER IX

SOLUBILITY PRODUCT

179. Solubility Product Principle. — The solubility product principle, enunciated by Nernst about 1889, is a relationship which is at the basis of all gravimetric procedure in that it generalizes *the behavior of slightly soluble electrolytes* [1] in their saturated solutions.[2] The importance of the principle lies in the fact that whenever we are concerned in bringing about precipitation or in preventing it, or in effecting solution, we are dealing with the very conditions of which this principle treats. The principle may be stated as follows: in a saturated solution of a slightly soluble electrolyte, the product of the concentrations of the constituent ions for any given temperature is sensibly a constant, the ion concentrations being raised to powers equal to the respective numbers of ions of each kind furnished by one mole of the electrolyte upon dissociating.

Thus, for the general case of the slightly soluble electrolyte A_mB_n, we would have as the numbers of ions of each kind which it would furnish upon dissociating, m cations and n anions according to the scheme:

$$A_mB_n \rightleftarrows mA^{+\cdots} + nB^{-\cdots}$$
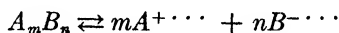
whence

$$[A^{+\cdots}]^m [B^{-\cdots}]^n = \text{solubility product of } A_mB_n.$$

The solubility product equation for AgCl is

$$[Ag^+][Cl^-] = K_{AgCl}$$

and for Ag_2CrO_4, it is

$$[Ag^+]^2 [CrO_4^=] = K_{Ag_2CrO_4}.$$

Table 33 gives the values for the solubility products of a variety of the more common slightly soluble electrolytes.

[1] Broadly speaking, most of the electrolytes considered under this category have a solubility less than 50 mg. per liter.

[2] A saturated solution of a substance is one in which the solute is in equilibrium with the solution.

Table 33

SOLUBILITY PRODUCTS

Compound	Temp. °C	Ions Involved	Solubility Product
Acetate			
Silver[3]	25	$[Ag^+][CH_3CO_2^-]$	4.4×10^{-3}
Argenticyanide			
Silver[4]	25	$[Ag^+][Ag(CN)_2^-]$	1.1×10^{-11}
Bromate			
Silver[5]	25	$[Ag^+][BrO_3^-]$	6.6×10^{-5}
Bromide			
Silver[6]	25	$[Ag^+][Br^-]$	7.7×10^{-13}
Cuprous[7]	18–20	$[Cu^+][Br^-]$	4.1×10^{-8}
Carbonate			
Barium[8]	25	$[Ba^{++}][CO_3^-]$	8.1×10^{-9}
Calcium[9]	25	$[Ca^{++}][CO_3^-]$	4.8×10^{-9}
Strontium[8]	25	$[Sr^{++}][CO_3^-]$	1.6×10^{-9}
Magnesium[10]	25	$[Mg^{++}][CO_3^-]$	1×10^{-5}
Lead[11]	18	$[Pb^{++}][CO_3^-]$	3.3×10^{-14}
Chloride			
Silver[12]	25	$[Ag^+][Cl^-]$	1.5×10^{-10}
Cuprous[7]	18–20	$[Cu^+][Cl^-]$	1.0×10^{-6}
Mercurous[13]	25	$[Hg_2^{++}][Cl^-]^2$	3.5×10^{-18}
Chromate			
Silver[14]	25	$[Ag^+]^2[CrO_4^-]$	2.4×10^{-12}
Lead[15]	18	$[Pb^{++}][CrO_4^-]$	1.8×10^{-14}
Barium[16]	18	$[Ba^{++}][CrO_4^-]$	1.6×10^{-10}
Strontium[14]	25	$[Sr^{++}][CrO_4^-]$	3.5×10^{-5}
Fluoride			
Calcium[14]	25	$[Ca^{++}][F^-]^2$	3.2×10^{-11}
Hydroxide			
Silver[17]	25	$[Ag^+][OH^-]$	2.3×10^{-8}
Magnesium[18]	18	$[Mg^{++}][OH^-]^2$	3.4×10^{-11}
Iodate			
Lead[19]	25	$[Pb^{++}][IO_3^-]^2$	1.9×10^{-13}
Iodide			
Silver[12]	25	$[Ag^+][I^-]$	0.9×10^{-16}
Cuprous[7]	18–20	$[Cu^+][I^-]$	5.0×10^{-12}
Oxalate			
Calcium[20]	25	$[Ca^{++}][C_2O_4^-]$	2.6×10^{-9}
Magnesium[16]	18	$[Mg^{++}][C_2O_4^-]$	8.6×10^{-5}
Phosphate			
Magnesium Ammonium[21]	25	$[Mg^{++}][NH_4^+][PO_4^{\equiv}]$	2.5×10^{-13}

Table 33 — *Continued*

Compound	Temp. °C	Ions Involved	Solubility Product
Sulfate			
Lead[22]	25	$[Pb^{++}][SO_4^=]$	2.2×10^{-8}
Barium[23]	25	$[Ba^{++}][SO_4^=]$	9.2×10^{-11}
Strontium[16]	17	$[Sr^{++}][SO_4^=]$	2.8×10^{-7}
Calcium[24]	25	$[Ca^{++}][SO_4^=]$	2.3×10^{-4}
Silver[25]	25	$[Ag^+]^2[SO_4^=]$	7.7×10^{-5}
Sulfide *			
Mercury[26]	25	$[Hg^{++}][S^=]$	4×10^{-54}
Silver[27]	18	$[Ag^+]^2[S^=]$	2×10^{-49}
Copper[28]	16–18	$[Cu^{++}][S^=]$	2×10^{-47}
Lead[28]	18	$[Pb^{++}][S^=]$	5×10^{-29}
Cobalt[27]	18	$[Co^{++}][S^=]$	3×10^{-26}
Nickel[27]	18	$[Ni^{++}][S^=]$	1×10^{-24}
Zinc[27]	18	$[Zn^{++}][S^=]$	1×10^{-23}
Iron[27]	18	$[Fe^{++}][S^=]$	4×10^{-19}
Thiocyanate			
Silver[29]	25	$[Ag^+][SCN^-]$	1.2×10^{-12}
Cuprous[18]	18	$[Cu^+][SCN^-]$	1.6×10^{-11}

* Approximate values.

[3] MacDougall and Bartsch, *J. Phys. Chem.*, **40**, 649 (1936).
[4] Randall and Halford, *J. Am. Chem. Soc.*, **52**, 178 (1930).
[5] Neuman, *J. Am. Chem. Soc.*, **56**, 28 (1934).
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[9] Frear and Johnston, *J. Am. Chem. Soc.*, **51**, 2082 (1929).
[10] Kline, *J. Am. Chem. Soc.*, **51**, 2093 (1929).
[11] M. Pleissner, *Arb. kaiser Gesundh.*, **26**, 30 (1907).
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[14] Seidell, "Solubilities of Inorganic and Organic Compounds," 2nd ed., D. Van Nostrand Co., Inc., New York, 1928.
[15] K. Beck, *Z. Elektrochem.*, **17**, 846 (1911).
[16] F. Kohlrausch, *Z. physik. Chem.*, **64**, 158 (1908).
[17] A. A. Noyes & D. A. Kohr, *Z. physik. Chem.*, **42**, 343 (1903).
[18] F. Kohlrausch & F. Rose, *Z. physik. Chem.*, **12**, 24 (1893).
[19] La Mer and Goldman, *J. Am. Chem. Soc.*, **52**, 2791 (1930).
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[22] Crockford and Brawley, *J. Am. Chem. Soc.*, **56**, 2600 (1934).
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[25] Harkins, *J. Am. Chem. Soc.*, **33**, 1807 (1911).
[26] J. Knox, *Z. Elektrochem.*, **12**, 480 (1906).
[27] L. Bruner & J. Zawadski, *Z. anorg. Chem.*, **67**, 455 (1910).
[28] G. Trümpler, *Z. physik. Chem.*, **99**, 49 (1921).
[29] F. W. Küster & A. Thiel, *Z. anorg. Chem.*, **33**, 139 (1903).

180. Solubility Product and Salt Effect. — From theoretical considerations we would expect the solubility product of a substance at a given temperature to be substantially a constant provided the total ion concentration remains constant. We would also expect the value of the solubility product to increase with the total ion concentration. Experimental determinations of the solubility product actually show such an increase. This is illustrated by the results of Jahn,[30] in Table 34. The solubility product of AgCl is seen to increase as the concentration of KCl is increased.

Table 34

EFFECT OF VARIATION OF TOTAL ION CONCENTRATION ON SOLUBILITY PRODUCT

Conc. of KCl	$[Cl^-]$	$[Ag^+]$	$[Ag^+][Cl^-]$
.00833	.00833	$.0_7139$	$.0_9116$
.01114	.01114	$.0_7107$	$.0_9119$
.01669	.01669	$.0_8738$	$.0_9123$
.03349	.03349	$.0_8388$	$.0_9130$

The solubility products given in Table 33 were determined in solutions in which the salt effect is negligible. Obviously, these values cannot be used for precise calculations in cases when there is considerable salt effect. When activities are used instead of concentrations in the solubility product equation, the value of K will not be affected by changes in total ion concentration. However, it is convenient to use concentrations rather than activities, and in succeeding discussions concentrations will be used except where activities are specifically indicated.

181. Solubility Product and Temperature. — An increase in temperature results in an increase in solubility of many precipitates. In such cases there is a corresponding increase in the value of the solubility product. For most precipitates dealt with in quantitative analysis, this variation for temperatures between 15° and 35° is so slight that we can ordinarily regard the value of the solubility product as being independent of temperature. A few exceptions to this rule will be noted in connection with certain determinations.

[30] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

In the case of hydrogen sulfide gas, an increase in temperature results in a decrease in solubility. Although the increase in temperature increases the ionization of dissolved hydrogen sulfide, the decrease in solubility is sufficient to produce a decrease in the value of the solubility product.

182. Calculation of Solubility Product from Solubility. — As an illustration of the calculation of the solubility product from the solubility, let us consider the case of AgCl. One liter of a saturated solution of this salt at 18° contains approximately 0.00143 g. Its molar solubility, S, can then be obtained from

$$S = \frac{0.00143}{143.3} = 1 \times 10^{-5}.$$

Since each mole of AgCl yields one mole of Ag^+ and one mole of Cl^-, we have
$$[Ag^+] = [Cl^-] = 1 \times 10^{-5}.$$

Substituting in the equation,

$$[Ag^+][Cl^-] = K_{AgCl},$$

we get
$$1 \times 10^{-5} \times 1 \times 10^{-5} = K_{AgCl} = 1 \times 10^{-10}.$$

For electrolytes yielding two ions from each mole, we see that

$$S^2 = K.$$

From this relationship we can calculate S if we know the value of K. From S and the molecular weight we can calculate the solubility in grams per liter, for

$$S \times \text{molecular weight} = \text{solubility in g./l.}$$

As a further illustration, let us consider the case of Ag_2CrO_4. The molar solubility of this salt is approximately 8×10^{-5}. Since each mole of Ag_2CrO_4 yields two moles of Ag^+, it follows that

$$[Ag^+] = 2 \times 8 \times 10^{-5} = 16 \times 10^{-5}.$$

Substituting in the solubility product equation,

$$[Ag^+]^2[CrO_4^-] = K_{Ag_2CrO_4},$$

we have
$$(16 \times 10^{-5})^2 \times 8 \times 10^{-5} = K_{AgCrO_4} = 2 \times 10^{-12}.$$

For uni-bivalent electrolytes, we see that

$$4S^3 = K.$$

183. Solubility Product an Ultimate Value Attained at Equilibrium. — The solubility product is in reality an ultimate value which is attained by the ionic product when equilibrium has been established between the solid phase of a slightly soluble salt and the solution. If affairs happen or can be arranged in any given case so that the ionic product is different from the solubility product, then the system will seek to adjust itself in such a way that the ionic product will attain the value of the solubility product. Thus, if the ionic product is arbitrarily made greater than the solubility product, as, for instance, through the addition of another salt with an ion in common, the adjustment of the system results in the precipitation of the solid salt. Conversely, if the ionic product is of itself smaller than the solubility product or can arbitrarily be made smaller, as, for instance, by the repression of the concentration of one of the ions, the adjustment of the system results in the solid salt going into solution.

To illustrate these ideas we will now give two examples. As our first example, let us consider the case of silver chloride to show the formation of a precipitate. If we add a solution of potassium chloride to a solution of silver nitrate, the chloride ion is momentarily present in such concentration that its ionic product with the silver ion exceeds the solubility product of silver chloride, and, consequently, the insoluble silver chloride is precipitated according to the reaction:

$$Ag^+ + Cl^- \rightleftharpoons AgCl \downarrow.$$
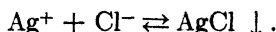
At the point at which we have added an equivalent amount of potassium chloride, granting that the system has reached equilibrium, the concentration of the silver ion will be equal to that of the chloride ion. Since

$$[Ag^+]\,[Cl^-] = 1 \times 10^{-10},$$

it follows that

$$[Ag^+] = [Cl^-] = 1 \times 10^{-5}.$$

If now, starting with such a saturated solution of silver chloride, we add either a soluble silver salt or a soluble chloride, we find that a slight further precipitation of silver chloride takes place, and if, after equilibrium has been attained, we measure the concentrations of the respective ions, we find that, although the

concentration of one has been increased and the concentration of the other decreased, nevertheless their product has roughly the same value as before. This is clearly shown in Table 34.

As our second example, let us apply the solubility product principle to the dissolving of a precipitate. In a saturated solution of calcium oxalate in contact with a precipitate of calcium oxalate, the following relationship exists:

$$[Ca^{++}] [C_2O_4^-] = K_{CaC_2O_4}.$$

By adding HCl to this solution we can form the complex ion $HC_2O_4^-$ by means of the following reaction:

$$C_2O_4^- + H^+ \rightarrow HC_2O_4^-,$$
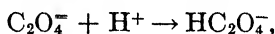
thereby decreasing $[C_2O_4^-]$. The product of the ion concentrations becomes less than $K_{CaC_2O_4}$ and the precipitate begins to go into solution. At equilibrium, the ion product is again equal to the solubility product.

184. Complex Ions and Solubility Product. — As seen in the illustration just given, the formation of a complex ion from one of the ions of the precipitate may bring about the dissolving of the precipitate. The relation of complex ion formation to the solubility product principle is of great importance in analytical chemistry and warrants further illustration. As an example, let us consider a precipitate of silver argenticyanide in contact with its saturated solution. This equilibrium can be represented as follows:
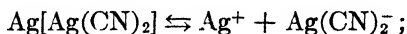
$$Ag[Ag(CN)_2] \leftrightarrows Ag^+ + Ag(CN)_2^- ;$$

where, according to the solubility product principle,

$$[Ag^+] [Ag(CN)_2^-] = 1.1 \times 10^{-11}.$$

The argenticyanide ion dissociates to some extent into Ag^+ and CN^-. At equilibrium we have

$$Ag(CN)_2^- \leftrightarrows Ag^+ + 2CN^-$$
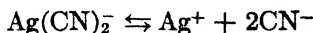
when, according to the law of mass action,

$$\frac{[Ag^+] [CN^-]^2}{[Ag(CN)_2^-]} = 4.5 \times 10^{-19}.$$

The silver ions in the solution are furnished not only by the precipitate but also by the dissociation of $Ag(CN)_2^-$. However, it is obvious from the very small value of the dissociation constant that relatively few silver ions result from this dissociation and practically all of them are furnished by the precipitate. It follows that although $[Ag^+]$ will be slightly larger than $[Ag(CN)_2^-]$, for all practical purposes we can consider that

$$[Ag^+] = [Ag(CN)_2^-] = 3.3 \times 10^{-6}.$$

Let us suppose that on adding KCN to this solution the reaction

$$Ag^+ + 2CN^- \rightarrow Ag(CN)_2^-$$
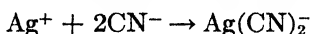
takes place until

$$[Ag^+] = 0.3 \times 10^{-6}.$$

Momentarily $[Ag(CN)_2^-]$ will be increased to 6.3×10^{-6}. Substituting these values in the solubility product equation for $Ag[Ag(CN)_2]$, we have
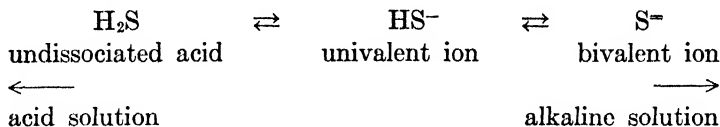
$$0.3 \times 10^{-6} \times 6.3 \times 10^{-6} = 1.89 \times 10^{-12}.$$

This product is less than the solubility product and consequently some of the precipitate will dissolve.

185. Rôle of Hydrogen Ion Concentration. — It will be found in almost every case where we are dealing with the solubility product principle that the hydrogen ion concentration of the solution enters into matters as a very important factor. This situation arises from the fact that the concentrations of anions, which we use to bring about precipitation, and those which we use to form complexes, are very greatly influenced by the concentration of hydrogen ion.

Taking up for our consideration, first, the more common examples of the anions used for precipitation, we see, in the case of hydroxyl ion, that its concentration varies inversely as the concentration of hydrogen ion by virtue of the relationship that $[H^+][OH^-] = 10^{-14}$. The concentration of bivalent anion, such as the sulfide ion, the carbonate ion or the sulfate ion, is affected by the concentration of hydrogen ion. At equilibrium, there is always present not only the bivalent anion but also the corresponding univalent ion and the undissociated acid, the particular

distribution of the respective concentrations depending on the concentration of hydrogen ion.   Thus, if we take the case of sulfide ion, we have the equilibrium represented by the scheme:

$$H_2S \quad \rightleftarrows \quad HS^- \quad \rightleftarrows \quad S^=$$

undissociated acid   univalent ion   bivalent ion

$\longleftarrow$ $\longrightarrow$

acid solution   alkaline solution

If now we alter the concentration of hydrogen ion, then the components toward the left-hand end of the equilibrium will predominate if the solution is made increasingly acid; while the components toward the right-hand end will predominate if the solution is made increasingly alkaline.   If a large concentration of H^+ is present in a solution from which ZnS is to be precipitated by means of the H_2S, $[S^=]$ may have a value so small that

$$[Zn^{++}]\,[S^=] < K_{ZnS}.$$

Consequently no precipitate will form.   By repressing $[H^+]$ we may bring about sufficient increase in $[S^=]$ so that

$$[Zn^{++}]\,[S^=] > K_{ZnS},$$

whereupon a precipitate will be produced as a result of the reaction
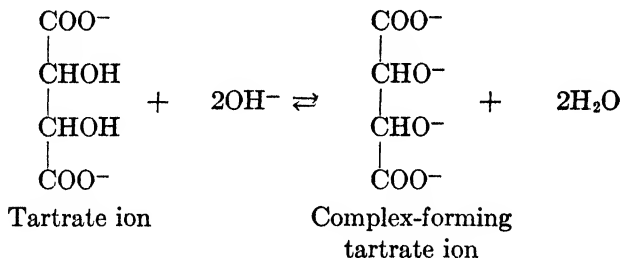
$$Zn^{++} + H_2S \rightarrow ZnS + 2H^+.$$
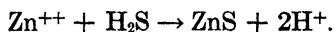
As has been pointed out in § 127 the increase in $[H^+]$ during this reaction may bring about equilibrium before the precipitation of Zn^{++} becomes quantitative.   A substantially constant $[H^+]$ may be maintained in the solution by means of a buffer as explained in § 127.

Coming now to the effect of the hydrogen ion concentration upon those anions which we use to form complexes with metal ions, we will select as illustrations the cases of the tartrate and the citrate ions because these find subsequent application in our laboratory work and their behavior is representative of a large class of organic compounds, such as the sugars, glycerine, etc., which contain alcohol groups.   All these substances, as far as their property of being able to form complexes is concerned, seem to function through one or more of their alcohol groups after the
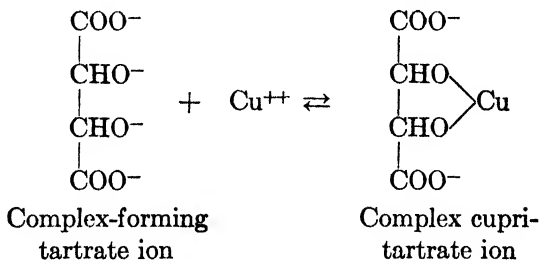
manner shown herewith for tartrate ion.   If we dissolve tartaric
acid or a salt of tartaric acid in water, we will have an equilibrium
between the undissociated acid and the tartrate ion, thus,

$$
\begin{array}{ccc}
\text{COOH} & & \text{COO}^- \\
| & & | \\
\text{CHOH} & & \text{CHOH} \\
| & \rightleftarrows & | \qquad + \qquad 2\text{H}^+ \\
\text{CHOH} & & \text{CHOH} \\
| & & | \\
\text{COOH} & & \text{COO}^-
\end{array}
$$

$$\text{Tartaric acid} \qquad\qquad \text{Tartrate ion}$$
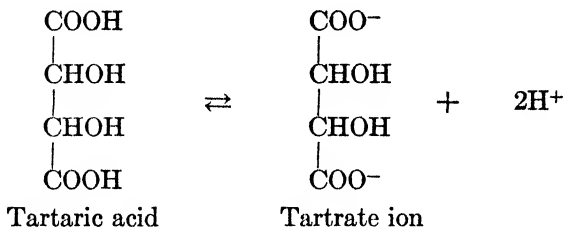
If now we make the solution alkaline, the alcohol groups ionize
according to the scheme

$$
\begin{array}{ccc}
\text{COO}^- & & \text{COO}^- \\
| & & | \\
\text{CHOH} & & \text{CHO}^- \\
| & + \quad 2\text{OH}^- \rightleftarrows & | \qquad + \qquad 2\text{H}_2\text{O} \\
\text{CHOH} & & \text{CHO}^- \\
| & & | \\
\text{COO}^- & & \text{COO}^-
\end{array}
$$

$$\text{Tartrate ion} \qquad\qquad \begin{array}{c}\text{Complex-forming} \\ \text{tartrate ion}\end{array}$$
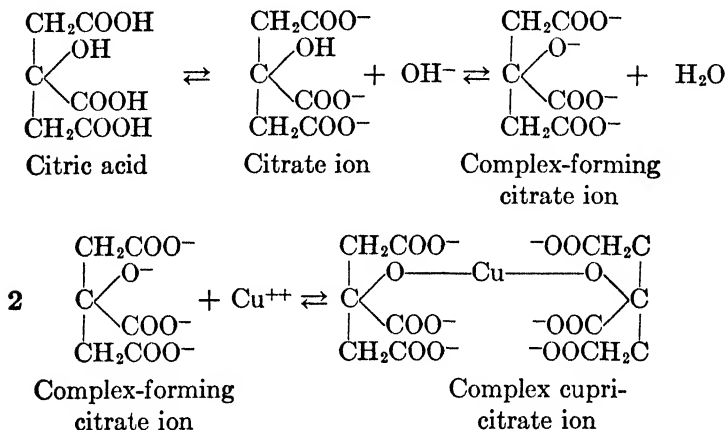
In the presence of a metal ion, the complex-forming tartrate ion
will unite with the metal ion to form a complex metal-tartrate
ion; thus, in the presence of cupric ion we have

$$
\begin{array}{ccc}
\text{COO}^- & & \text{COO}^- \\
| & & | \\
\text{CHO}^- & & \text{CHO} \\
| & + \quad \text{Cu}^{++} \rightleftarrows & | \quad \!\!\!\!\!\!\!\! \diagdown \\
\text{CHO}^- & & \text{CHO} \quad \!\!\!\!\!\!\!\! \diagup \text{Cu} \\
| & & | \\
\text{COO}^- & & \text{COO}^-
\end{array}
$$

$$\begin{array}{c}\text{Complex-forming} \\ \text{tartrate ion}\end{array} \qquad\qquad \begin{array}{c}\text{Complex cupri-} \\ \text{tartrate ion}\end{array}$$

For any given complex-forming organic ion the extent to which
a metal ion becomes tied up depends upon the alkalinity of the
solution and the nature of the metal ion.   For instance, in a

solution which was 0.166 M with respect to potassium-sodium tartrate and 0.033 M with respect to copper sulfate, Immerwahr [31] found that the concentration of cupric ion at 18° was 2.3×10^{-9}.

In an analogous way, the mechanism of complex ion formation for citric acid is as follows:

CH₂COOH   CH₂COO⁻   CH₂COO⁻

Citric acid   Citrate ion   Complex-forming citrate ion

Complex-forming citrate ion   Complex cupri-citrate ion

186. Solubility Product Makes No Mention of Rate of Attainment of Equilibrium. — It is to be noticed that the solubility product defines a state of equilibrium but makes no mention of the rate at which equilibrium is attained. While it is a necessary condition that the solubility product be exceeded in order to bring about precipitation, it is no guarantee that precipitation will take place at once. In point of fact, in the formation of small amounts (say up to 5 mg.) of a great many of our insoluble salts, such as barium sulfate, ammonium phosphomolybdate, magnesium ammonium phosphate, and copper sulfide, it takes from 14 to 48 hours before precipitation is ended and equilibrium is reached. Hence the statement so often made, that exceeding the solubility product causes precipitation, must be taken with the important qualification that for small amounts of precipitates a certain time must elapse before precipitation begins, and then a further and often considerable period must elapse before precipitation is completed.

[31] Immerwahr, *Z. anorg. Chem.*, **24**, 269 (1900).

187. Complete Precipitation Impossible. — It should be pointed out at this juncture that, while we can precipitate almost all of a slightly soluble electrolyte, complete precipitation is impossible because no matter how much we arbitrarily increase the concentration of one ion, we cannot decrease the concentration of the other to zero, by virtue of the fact that the solubility product is a constant.   This idea can perhaps best be brought out if we depict the relationship graphically, using the respective ionic concentrations as coördinates. The graph will be an equilateral hyperbola for simple electrolytes of the 1:1 type like silver chloride, and there will be similar curves for the other types of salts, namely, 1:2, 1:3, 2:3, etc.   From the properties of the equilateral hyperbola we know that it never intersects the coördinate axes but becomes sensibly parallel to them. This idea can be visualized from Figure 45.   An important corollary which follows is that, after a certain point, further excess of precipitant accomplishes no material benefit in the further throwing out of the precipitate.   As a matter of fact, a large excess of precipitant may actually cause some of the precipitate to dissolve either as a result of complex-ion formation with an ion of the precipitate or as a result of increased salt effect.   The effect which a large excess of NaCl has on the solubility of AgCl is shown by the results of Forbes,[32] given in Table 35.

Fig. 45

Relationship of the Concentration of Silver Ion to That of Chloride Ion in Saturated Solutions of Silver Chloride

On the basis of the solubility product principle, the completeness of precipitation accomplished by a moderate excess of precipitant can be determined, approximately, if we know the value of the solubility product and the concentration of excess
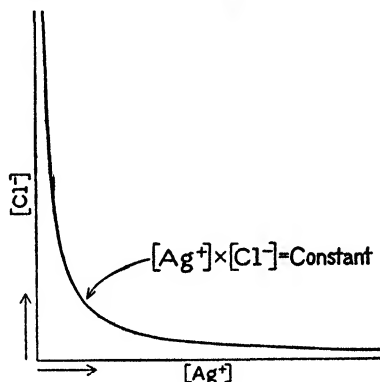
[32] Forbes, *J. Am. Chem. Soc.* **33**, 1937 (1911).

precipitant. If Ag^+ is precipitated from solution by adding Cl^- until $[Cl^-] = 2 \times 10^{-3}$, it follows that

$$[Ag^+] \times 2 \times 10^{-3} = 1 \times 10^{-10},$$

and

$$[Ag^+] = \frac{1 \times 10^{-10}}{2 \times 10^{-3}} = 5 \times 10^{-8},$$

and the weight in grams per liter of unprecipitated silver will be

$$107.9 \times 5 \times 10^{-8} = 5.4 \times 10^{-6} \text{ g. per liter.}$$

Table 35

EFFECT OF NaCl ON SOLUBILITY OF AgCl

NaCl Moles/Liter	Ag Moles/Liter
0.933	0.000086
1.433	0.000184
2.272	0.000570
3.000	0.001194
4.170	0.003335
5.039	0.006039

188. Non-aqueous Solvents. — Some analytical separations cannot be performed quantitatively by precipitation from a water solution, due to the fact that the elements to be separated do not form compounds having a sufficiently wide difference in solubility. By way of illustration, let us suppose that a precipitate consists of a mixture of $Na_2PtCl_6 \cdot 6H_2O$ and K_2PtCl_6 and that it is required to separate the sodium from the potassium. Addition of water would dissolve both components whereas addition of 80% alcohol causes the $Na_2PtCl_6 \cdot 6H_2O$ to go into solution but leaves the K_2PtCl_6 as a residue. In general, addition of alcohol to water diminishes the solubility of inorganic precipitates. By adding the correct amount of alcohol in a given case it may be possible to render one component in a precipitate negligibly soluble, whereas the other component, although its solubility is also diminished by the alcohol, remains sufficiently soluble so that it may be removed. The change in the nature of the solvent finds other important uses in analytical separations.

Additional examples of uses of non-aqueous solvents are given in Chapter XIV.

189. Fractional Precipitation. — So far we have discussed the solubility product principle in relation to the case where one insoluble salt is formed. Let us now extend the discussion to the case where several slightly soluble salts are to be considered, because this is the usual situation which is met with in gravimetric separations. There are two general situations which arise, namely,

1. That in which the salts behave independently, and the solubility product principle can be applied rigidly to the behavior of each salt in the same manner as it could if the other salts were not present. Relatively few cases come under this category.

2. That in which the salts do *not* behave independently and the solubility product principle can be applied only in a qualitative way to their behavior. Most of the cases come under this category.

As an example coming under the first category, we will mention the case of silver chloride and silver chromate.[33] The respective solubility product equations are

$$[Ag^+]\,[Cl^-] = 1 \times 10^{-10}$$
$$[Ag^+]^2\,[CrO_4^-] = 2 \times 10^{-12}.$$
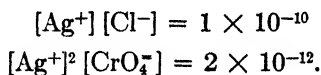
For the condition of equilibrium between the two precipitates and their supernatant liquid, these two relationships must be satisfied simultaneously. By squaring the solubility product equation for AgCl and dividing by that for Ag_2CrO_4, we can eliminate the silver ion concentration and obtain the following equilibrium ratio between the concentrations of chloride ion and chromate ion.

$$\frac{[Cl^-]^2}{[CrO_4^-]} = \frac{1}{2 \times 10^8}.$$

[33] The classic method of Mohr for determining chlorides by titration with silver nitrate solution, using sodium or potassium chromate as indicator, is based upon the independence of behavior of silver chloride and silver chromate. The application of the theory works out so beautifully in its detail that the authors have deemed it well worth-while for the benefit of the student to present it more fully in § 206.

If we start with a solution of a soluble chloride and a soluble chromate in equivalent quantities and add a solution of silver nitrate dropwise, then silver chloride will be precipitated alone[34] until the chromate ion is in the excess indicated by the equilibrium ratio; after this, silver chromate will be precipitated with traces of silver chloride, the equilibrium ratio between the chloride and chromate ions in the supernatant liquid being maintained. If, on the other hand, we start with a solution containing a concentration of chromate ion greater than that required by the equilibrium ratio, then silver chromate will be precipitated first until the ratio is reached. The more important cases in elementary analysis, where two or more slightly soluble salts behave independently, are as follows: silver chloride and silver chromate, silver chloride, silver bromide and silver iodide, antimony sulfide and stannic or stannous sulfide.

As an example coming under the second category, we will mention the precipitation of copper and zinc as sulfides. If we have a solution of a soluble copper salt and adjust the concentration of hydrogen ion so that it is equivalent to 0.3 M HCl, and then pass in hydrogen sulfide until the solution is saturated, the copper will be quantitatively precipitated as copper sulfide. If, on the other hand, we have a solution of a soluble zinc salt and adjust the concentration of hydrogen ion so that it likewise is equivalent to 0.3 M HCl, and then pass in hydrogen sulfide, there will be no precipitate of zinc sulfide because the solubility product has not been reached. Suppose now that we have a third solution containing both the soluble copper salt and the soluble zinc salt and adjust the concentration of hydrogen ion to the same value as before and pass in hydrogen sulfide; the copper will be quantitatively precipitated as the sulfide and along with it more or less zinc sulfide, even though the solubility product of the latter has not been reached. The zinc sulfide which contaminates the copper sulfide precipitate cannot be dissolved out of or separated from the rest of the precipitate. Apparently, much of it is held by some kind of chemical union and is not present merely as an admixture.

[34] If silver chromate is momentarily precipitated at this juncture it will be converted into the chloride.

190. Co-precipitation. — When a solute present in insufficient concentration to supersaturate a solution is nevertheless removed from the solution as a contaminant of a precipitate, we say that this solute has been *co-precipitated*. Co-precipitation is very frequently encountered in analytical separations and is a very common source of experimental error. A few of the more important cases in which one slightly soluble salt drags down another are listed herewith:

Salt precipitated	*Slightly soluble salt dragged down*
Copper sulfide	Zinc sulfide
Cadmium sulfide	Zinc sulfide
Chromium hydroxide	Zinc hydroxide
Ferric hydroxide	Copper hydroxide from ammoniacal solution
Silicic acid	Aluminum hydroxide, ferric hydroxide

It must also be mentioned that the phenomenon of co-precipitation or dragging down is not limited to the case of one slightly soluble salt dragging down another but also extends to the dragging down of salts which are very soluble, as, for instance, the dragging down of ferric sulfate by barium sulfate, or of sodium oxalate by calcium oxalate. It is also true for these cases that the salt which is dragged down, notwithstanding its solubility otherwise, cannot be dissolved out of the precipitate. A list of the more frequent cases which are encountered in regard to the dragging down of soluble salts is given herewith:

Salt precipitated	*Soluble salt dragged down*
Barium sulfate	Ferric sulfate, potassium sulfate, barium nitrate, calcium nitrate
Aluminum hydroxide	Aluminum sulfate
Calcium oxalate	Magnesium oxalate
Magnesium ammonium phosphate	Ammonium molybdate
Nickel diacetyl-dioxime	Copper diacetyl-dioxime

The outstanding facts about the phenomenon of co-precipitation, so far as our present-day knowledge goes, are these:

1. The action is specific.
2. Co-precipitation may take place at the time of the formation of the precipitate.
3. Co-precipitation may also take place after the precipitate has formed.
4. The amount of co-precipitation is a function of the concentration of the salt dragged down.
5. The amount of co-precipitation is often affected by degree of supersaturation of substances being precipitated.

191. Specificity of Co-precipitation. — This characteristic is represented by the illustrations cited above of the effect of copper sulfide precipitate in causing the co-precipitation of zinc sulfide. It is not yet possible from theory to say with certainty beforehand, in the case of two salts, whether one will drag down the other, or, in the case of several salts, how any one of them will influence the others; such information must be supplied by experiment. In general, it has been found that the more closely an ion resembles one of the ions of the precipitate, the more likely it is that it will be co-precipitated. It has been found by Paneth, Fajans and Hahn that the more insoluble the compound containing an ion in common with the precipitate, the greater the extent of co-precipitation of this compound by the precipitate.

192. Concomitant Occurrence of Co-precipitation. — There seems to be scarcely any doubt that considerable co-precipitation takes place simultaneously with the formation of the slightly soluble salt. While the quantitative evidence bearing on this fact is not so extensive as might be desired, such evidence as we have points to its firm establishment. A series of experiments by Blasdale [35] upon the precipitation of barium sulfate is highly corroborative. This investigator carried out experiments in duplicate as follows: 25 ml. of a solution of sulfuric acid containing exactly 0.4250 g. of H_2SO_4 was used, which should, therefore, yield exactly 1.0118 g. of $BaSO_4$; 1.000 g. of KNO_3 was added, the solution was diluted to exactly 200 ml., heated to boiling, and the $BaSO_4$ precipitated by the addition of 50 ml.

[35] W. C. Blasdale, p. 138, for reference see § 11.

of a solution containing 1.3 g. of $BaCl_2$; after standing for sixteen hours the precipitate was filtered off, washed thoroughly, ignited and weighed. Another determination in duplicate was made in the same manner as above except that the 1.000 g. of KNO_3 was added after the precipitant had been added and the mixture had been allowed to stand for ten minutes. A control determination in duplicate was also made without the presence of any potassium nitrate. The several results are given herewith in Table 36.

Table 36

CO-PRECIPITATION CONCOMITANT WITH PRECIPITATION

	KNO_3 Added Before Precipitation of $BaSO_4$	KNO_3 Added After Precipitation of $BaSO_4$	Control Determination with no KNO_3
Wt. of KNO_3 present...	1.0000 g.	1.0000 g.	0.0000 g.
Wt. of ppt. found (A)...	1.0308	1.0140	1.0131
Wt. of ppt. found (B)...	1.0291	1.0144	1.0134
Average of A and B.....	1.0300	1.0142	1.0133
Excess of wt. found.....	0.0182	0.0024	0.0015

By a comparison of the figures of the second and third columns, it is seen that the co-precipitation of the potassium nitrate is very small when this salt is added after the barium sulfate has been precipitated from the solution.

193. Co-precipitation Subsequent to the Formation of the Precipitate. — Considerable evidence has been obtained to show that co-precipitation may occur after the precipitate has formed. Braithwaite and Fales [36] precipitated CuS from a solution containing Cu^{++} and Zn^{++} and allowed the precipitate to stand in contact with the solution for some time. They showed that the amount of ZnS contaminating the CuS precipitate increased with the time of digestion. Kolthoff and Sandell [37] shook calcium oxalate monohydrate with potassium sulfate solution and brought about contamination of the precipitate with calcium sulfate.

[36] Braithwaite, Dissertation, Columbia University, 1925.
[37] *J. Am. Chem. Soc.*, **55**, 2170 (1933).

Some cases of contamination of precipitates subsequent to precipitation may be explained by saying that at the time of precipitation the solubility product of the co-precipitated substance was exceeded but that the rate of precipitation was extremely slow so that the amount of this material contaminating the precipitate increased appreciably with digestion. Some cases of contamination after precipitation may be the result of foreign ions in the solution entering the lattice of the precipitate or becoming attached to the surface of the precipitate when the solubility product of the co-precipitated substance has not been exceeded.
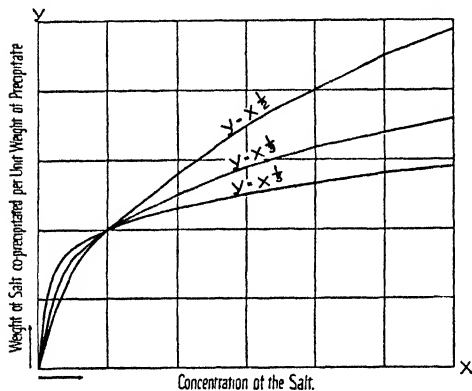
Fig. 46

Weight of Salt Co-precipitated per Unit Weight of Precipitate as a Function of the Concentration of Salt

194. *Variation of Co-precipitation with the Concentration of the Soluble Salt.* — For a given weight of precipitate, the amount of co-precipitation varies with the concentration of the soluble salt. The amount, however, is not directly proportional to such concentration but varies as some fractional power $1/n$, where n usually has the value two, and in no case apparently has a value less than unity or greater than five. The relationship expressed in the form of an equation is:

$$\frac{\text{Weight of salt dragged down}}{\text{Weight of precipitate}} = k(\text{concentration of salt})^{\frac{1}{n}} \quad (1)$$

where the value of k is determined by experiment. Equation (1) is analogous to Freundlich's equation for adsorption,[38] namely,

$$\frac{\text{Weight of substance adsorbed}}{\text{Weight of adsorbing agent}} = \frac{k(\text{equilibrium conc. of adsorbed substance})^{\frac{1}{n}}}{} \quad (2)$$

[38] H. Freundlich, "Kapillarchemie." Vol. I, p. 156. Akademische Verlagsgesellschaft. Leipzig, 1930.

Equation (1), however, in the light of our present-day knowledge, is to be regarded only as an empirical portrayal of the behavior of co-precipitation and not as a consequence of any theoretical deductions. In order to visualize the relationship expressed by equation (1) which gives the weight of salt dragged down per unit of precipitate y as a function of the concentration of the salt x, let us plot the curves

$y = kx^{\frac{1}{n}}$ for $k = 1$ and $n = 2, 3$, and 5; we get the curves given in Figure 46. All these curves are generalized parabolas.

A specific example is furnished from the work of Blasdale cited in § 192 upon the co-precipitation of potassium nitrate by barium sulfate. In addition to the experiments quoted there, this investigator also ran two others under similar conditions, der similar conditions, and with the addition of the potassium nitrate beforehand. The results are given in Table 37.
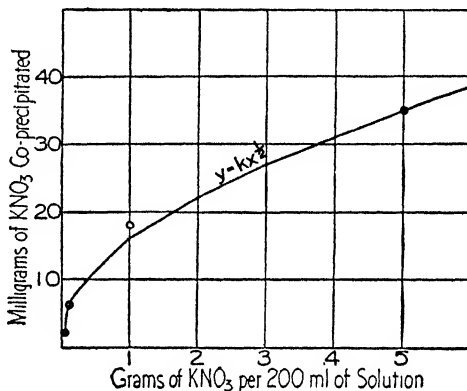
Fig. 47

Milligrams of KNO_3 Co-precipitated per Gram of $BaSO_4$ as a Function of Concentration of KNO_3

Table 37

EFFECT OF CONCENTRATION OF SOLUBLE SALT ON CO-PRECIPITATION

	0.2000 g.	5.0000 g.
Wt. of KNO_3 present	0.2000 g.	5.0000 g.
Wt. of ppt. found (A)	1.0199	1.0476
Wt. of ppt. found (B)	1.0160	1.0468
Average of A and B	1.0180	1.0472
Excess of wt. found	0.0062	0.0354

Plotting the results of all four experiments, we see that they sensibly satisfy the relationship $y = kx^{\frac{1}{2}}$, where $k = 15.6$, as shown by the graph of Figure 47.

195. *Co-precipitation and Degree of Supersaturation.* — It is often observed that a solution which contains the ions of a precipitate in sufficient concentrations to produce a high degree of supersaturation often yields a precipitate which is contaminated to a considerable extent as a result of co-precipitation. Under these conditions the precipitate forms rapidly and consists of very small particles possessing a very large surface. The increase of surface of the precipitate with an increase in the extent of supersaturation of the solution has been demonstrated by von Weimarn [39] by precipitating $BaSO_4$ from solutions containing a variety of concentrations of Ba^{++} and $SO_4^{=}$. It has also been shown that the actual particle size produced by a given degree of supersaturation depends to a considerable extent on the substance being precipitated. If one of the ions of the precipitant or some other ion in the solution is capable of contaminating the surface of the precipitate, we should expect that the greater the extent of surface and the greater the concentration of the contaminating ion, the greater the amount of co-precipitation. By producing a smaller degree of supersaturation by employing smaller concentrations of precipitating ions, we find that we can often materially diminish co-precipitation.

196. Colloidal Solutions. — When the solubility product of a slightly soluble electrolyte has been exceeded and particles of the precipitate begin to form, they may flocculate into particles of larger and larger dimensions and finally separate from the solution. Under some conditions, however, although the solubility product has been exceeded, no solid actually separates and the resulting solution exhibits properties which it did not previously possess. Many solutions of this sort are capable of scattering light at right angles to an incident beam, whereas the original solution does not produce this effect. This scattering of light, known as the *Tyndall effect,* may be accounted for by considering that the solution contains solute particles considerably larger than molecular dimensions. A convenient unit of measure in dealing with small particles is the $m\mu$, which is 0.000001 mm. The

[39] P. P. von Weimarn, "Zur Lehre von den Zustanden der Materie," Bd. I; Bd. II, Th. Steinkopff, Dresden, 1914; "Die Allgemeinheit des Kolloiden Zustandes," Th. Steinkopff, Dresden, 1925.

particles in solutions exhibiting the Tyndall effect probably have diameters larger than $10m\mu$. Such solutions are known as colloidal solutions. There are many situations in analytical chemistry where it is desirable to have a precipitate separate as completely as possible from solution. In such cases the formation of a colloidal solution is definitely a source of error. Precipitates obtained from colloidal solutions may be contaminated to a considerable extent, due to the large surface of the colloid particles. By preventing the formation of colloids, much of this contamination and its accompanying error may be avoided. It is desirable, therefore, for the analytical chemist to understand the causes of colloid formation and to know how the colloidal condition can be prevented, removed, or controlled.

When a current is passed through many colloidal solutions, the colloid particles migrate toward one of the electrodes, indicating that they are electrically charged. In some cases the charged particle may be formed by a combination of many complex ions, whereas in other cases the colloid particle may become attached to ions from the solution and thus acquire an 'electric charge. Precipitation is brought about in many colloids by the addition of electrolytes. The effectiveness of an electrolyte in producing precipitation usually depends to a considerable extent on the valence of the ion of the electrolyte which is opposite in sign to the charge on the colloid particle, trivalent ions being more effective than bivalent ions and these, in turn, more effective than univalent ions. In some cases stirring or the application of heat tends to bring about separation of the precipitate. Precipitation of colloids by electrolytes has many applications in analysis.

When precipitation has been produced and the precipitate subsequently filtered and washed with water, the concentration of electrolyte in the solution in contact with the precipitate may be diminished to the point where the precipitate begins to return to the colloidal condition. In many instances this can be avoided by using wash water containing a suitable electrolyte. Needless to say, it should be an electrolyte which does not form insoluble substances with ions in the solution, and, what is equally important, it must not form complex ions with the ions of the precipitate.

197. Theory of Co-precipitation. — The phenomenon of co-precipitation is a complex one and at present our insight into its mechanism is but slight. Schneider [40] has suggested that the salt which is co-precipitated is taken up by the precipitate as the latter is formed, and remains distributed throughout the interior of the solid particles; that is to say, co-precipitation is the result of the formation of a solid solution in which the precipitate is the solvent and the co-precipitated salt the solute. In accordance with this view, experiments by Walden and Cohen [41] have shown that when $BaSO_4$ is precipitated from solutions containing the nitrate ion, much of the $Ba(NO_3)_2$ which is co-precipitated probably occurs in the crystal lattice of the $BaSO_4$.

Ostwald has stated that an attractive or restraining force is exerted by the solid, which tends to hold the molecules of the co-precipitated substance in the immediate neighborhood of its boundary surfaces, and either delays or entirely prevents the removal of these substances by washing. This is the same theory which was advanced by E. du Bois Reymond under the title "adsorption" to characterize the retention of soluble substances by porous or finely divided solids when the latter are placed in solutions of the former. The well known property of bone-charcoal of removing coloring matter from solutions is a good illustration of adsorption. When the precipitate is a salt, the adsorption of ions can be accounted for, in part at least, on the basis of attraction between oppositely charged ions. Figure 48 represents a surface of a crystal of AgCl. An atom beneath the surface of the crystal exerts an attractive force on the six oppositely charged ions around it, whereas an ion at the surface, having no oppositely charged ion above it, has presumably a residual valence by means of which it can hold ions of opposite charge. If the

$$Ag^+ \; Cl^- \; Ag^+ \; Cl^- \; Ag^+$$
$$Cl^- \; Ag^+ \; Cl^- \; Ag^+ \; Cl^-$$
$$Ag^+ \; Cl^- \; Ag^+ \; Cl^- \; Ag^+$$
$$Cl^- \; Ag^+ \; Cl^- \; Ag^+ \; Cl^-$$
$$Ag^+ \; Cl^- \; Ag^+ \; Cl^- \; Ag^+$$

Fig. 48

Surface of Silver Chloride Crystal

[40] F. Schneider, *J. Am. Chem. Soc.*, **59**, 354 (1937).

[41] M. U. Cohen, Dissertation, Columbia University, 1935.

solution from which the AgCl was precipitated contains K^+ and NO_3^-, then Ag^+ at the surface of the precipitate might hold NO_3^- or some other negative ion present in the solution, and Cl^- at the surface of the precipitate might hold K^+ or some other positive ion.

Richards has stated that the phenomenon of co-precipitation is due to chemical rather than physical forces, and termed it "occlusion." According to this theory, complex basic salts or molecular compounds which are but slightly soluble are formed to a greater or less extent along with the desired precipitate. Thus the co-precipitation of ferric salts by barium sulfate is explained on the assumption that the latter precipitate contains small amounts of a double sulfate of the formula $BaSO_4 \cdot Fe_2(SO_4)_3 \cdot H_2O$. When this compound is ignited, the ferric sulfate is decomposed, and three molecules of SO_3 and one of water are expelled, one molecule of $BaSO_4$ and Fe_2O_3 being left behind. The results for the determination of SO_4 are therefore low even though the precipitate is contaminated with Fe_2O_3.

Co-precipitation has also been explained in some cases by supposing that, during the formation of crystals of precipitate, some of the solution has been mechanically enveloped by the precipitate.

Before much can be said concerning the fundamental principles of co-precipitation, a great deal of experimental data must be obtained by precise methods on individual cases of co-precipitation. It may be possible that solid solution formation, adsorption, occlusion and mechanical mixing each play an important part under certain conditions in producing co-precipitation.

198. Minimization of Co-precipitation. — An analysis of the facts in regard to co-precipitation shows that in order to cut down the amount of co-precipitation which happens at the time of formation of a precipitate, *matters must be so arranged that the concentration of the salt which is co-precipitated shall be as small as practicable*. If this salt already exists in the solution and cannot be removed by any ready means like evaporation, or by conversion into an insoluble compound, then the solution should be made as dilute as allowable before adding the precipitant. If the precipitant itself is co-precipitated or leads to

the formation of any soluble salt which is co-precipitated, then the precipitant should be diluted and added dropwise, especial care being taken that the solution — where precipitation is being effected — shall be vigorously stirred meanwhile. In certain cases of co-precipitation recourse is had to the expedient of dissolving the contaminated precipitate and reprecipitating; this procedure, which is known as *double precipitation,* is invariably followed in rock analysis where most of the salts encountered are those of members of the iron and aluminum or the alkaline earth groups.

The formation of a colloid with its extremely large surface area may often bring about considerable co-precipitation. By controlling conditions so as to avoid colloid formation, we may often avoid much contamination of the surface of the solute and much co-precipitation at the time of precipitation.

The amount of co-precipitation which exists after the formation of a precipitate can often be reduced somewhat by the process of digestion. If the precipitate is very finely divided and consequently has a large surface area, there is a possibility of considerable co-precipitation due to adsorption. As pointed out in § 24, small particles of a precipitate have a greater solubility than large particles, so that it is possible by means of digestion to cause the smaller particles to dissolve and crystallize on the larger particles. In this way the surface area of the precipitate is diminished and co-precipitation due to surface adsorption may sometimes be decreased. It should be borne in mind that in some cases co-precipitation continues after precipitation. Digestion might actually increase the error due to contamination in such cases.

Digestion of precipitates or washing of precipitates with solutions containing ions which may replace the co-precipitated ions in the precipitate and which can be subsequently removed by volatilization is sometimes resorted to in an attempt to diminish co-precipitation. Thus, AgI, precipitated with an excess of I^- from a solution containing K^+, may be contaminated with KI. On digesting or washing with a solution containing H^+, the co-precipitated K^+ may be replaced to some extent by H^+. HI can then be removed by volatilization. In a similar manner, K^+ can be replaced by NH_4^+ and the resulting NH_4I removed by means of heat.

199. Separation of Precipitate from Supernatant Solution. — The technique of effecting this separation has already been discussed, in § 29; the only points to be considered here are the application of the solubility product principle and our knowledge of the properties of colloids to the selection of the wash solution. Since a precipitate is more soluble in pure water than in a solution which contains an ion in common, it is advisable wherever practicable to employ a wash solution of this description. Thus, lead sulfate is washed with a 0.1 M solution of sulfuric acid;[42] copper sulfide with a 0.3 M solution of hydrochloric acid saturated with hydrogen sulfide; ferric hydroxide with a solution which is 0.1 M with respect to ammonium nitrate and 0.01 M with respect to ammonium hydroxide; ammonium phospho-molybdate with a 0.1 M solution of ammonium nitrate; etc. The use of such solutions, however, is limited by the following considerations: the salt which furnishes the ion in common must not leave a non-volatile residue if the precipitate is to be subsequently ignited, nor may it contain an ion that would form an insoluble compound with any of the ions of the supernatant solution from which the precipitate was formed, nor may it contain a complex-forming ion that would enter into combination with either ion of the precipitate. Wherever such restrictions do not apply, the method is a desirable one. It should be mentioned that there are a great many precipitates which can only be washed with a wash solution containing an electrolyte, because, if the attempt is made to wash them with pure water, they will pass into the colloidal condition and run through the filter paper.

200. *Use of a Saturated Solution of the Precipitate Itself as Wash Solution.*[43] — "It has sometimes been recommended to wash a precipitate with a *saturated* aqueous solution of the precipitate itself, in place of with pure water. It was reasoned that the solution, being already saturated with the salt, would not be able to dissolve any of the precipitate obtained. That is true; but if a saturated solution of a salt, *MeX*, is placed on a filter still holding an excess of the precipitant, *i.e.*, one of the ions, say X, of the precipitate, then this excess may cause super-

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[42] The sulfuric acid is then got rid of by washing with 95% alcohol.

[43] This paragraph quoted verbatim from Stieglitz, p. 149, see § 11.

saturation of the saturated washing fluid and some of the salt may be precipitated out of the washing fluid. The method, as commonly employed, has therefore the inherent fault, theoretically at least, of being liable to give too high results. If it is to be employed without error, precautions must be taken first to remove, from the precipitate and filter, the mother liquor (containing the excess of precipitant) as completely as possible. If in a given case this can be accomplished, then the danger of precipitating any of the salt (MeX) from the saturated solution is avoided, and the precipitate $(MeX \downarrow)$ may then be further washed with a saturated solution of the same salt (MeX), with advantage, in certain cases. Thus, in the Lindo-Gladding method [44] of determining potassium in the form of potassium chloroplatinate, the source of error, just discussed, has been avoided in the following way: the excess of precipitant, chloroplatinic acid H_2PtCl_6, which has the ion $PtCl_6^=$ in common with the precipitate, *is first removed* from the precipitate by thorough washing of the precipitate with alcohol; subsequently, other impurities, *e.g.*, sulfates, soluble in water but not in alcohol, are washed out with an aqueous solution of ammonium chloride [45] that has been saturated with potassium chloroplatinate. The method gives good results."

201. Examples.

1. What is the maximum concentration of hydroxyl ion that can be present in a 0.1 M solution of magnesium sulfate without precipitating magnesium hydroxide?

2. The solubility product of ferric hydroxide is 1.1×10^{-36}. What concentration of Fe^{+++} will be in equilibrium with precipitated $Fe(OH)_3$ in the presence of (0.1 M NH_4OH) + (0.2 M NH_4Cl)?

3. Assuming that you have 0.200 g. sulfate ion in a volume of 350 ml. and add 25 ml. 0.1 M barium chloride solution, (1) what will be the concentration of the sulphate ion after precipitation has been effected? (2) what will be its actual weight?

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[44] "Official Methods of Analysis," U. S. Dept. Agr., Bulletin 107, p. 11.

[45] The excess of chloroplatinic acid is first washed out of the precipitate primarily to avoid subsequent precipitation of ammonium chloroplatinate, but its removal also avoids the error discussed in the text.

4. Calculate the pH at which 0.1 M Ag$^+$ will be precipitated as silver oxide.

5. The solubility of calcium fluoride is 0.0163 g. per liter and that of calcium carbonate is 0.0110 g. per liter. In a given solution of a soluble calcium salt, which will cause the most complete precipitation of the calcium, the addition of fluoride ion until its concentration in solution is 0.1 mole per liter, or the addition of carbonate ion until its concentration in the solution is 0.1 mole per liter? Give in full your method of reasoning.

6. The ionization constant for acetic acid is 1.8 times ten to the minus fifth power. Methyl orange changes from yellow to pink at a hydrogen ion concentration approximately equal to ten to the minus fourth power. How much must 0.01 M acetic acid be diluted in order to show practically a neutral reaction with methyl orange?   Ans.   15.3 times.

7. Calculate the concentration of hydroxyl ion in a solution at 18° which is 0.5 M with respect to acetic acid.

8. Using acetic acid and sodium acetate as an example, verify the rule of Osaka, in *Coll. Sci. & Eng. Mem.*, **1**, 103 (1905); **3**, 205 (1907), that the concentration of hydrogen ion in a solution of a weak acid that is half neutralized by a strong base is equal to the numerical value of the ionization constant.

9. What is the concentration of hydrogen ion in a solution which is 0.01 M with respect to ammonium hydroxide?   Ans.   pH = 10.63.

10. The ionization constant for ammonium hydroxide is 1.8×10^{-5}. What is the concentration of hydrogen ion in a 0.2 M solution of ammonium hydroxide, which is also 0.1 M with respect to ammonium chloride?

11. A saturated solution of hydrogen sulfide at 25° contains approximately 3.4 g. H$_2$S per liter. The ionization constant for H$_2$S is 1.1×10^{-22}. What is the concentration of sulfide ion in a saturated solution of H$_2$S in the presence of 0.1 M HCl?

12. The ionization constant of formic acid is 2.1×10^{-4}. What concentration of hydrogen ion is furnished by 20 ml. of 5 M formic acid and 10 ml. 5 M sodium formate made up to 100 ml.?

13. The solubility product of silver sulfate at 25° is 7.7×10^{-5}. Calculate its solubility in milligrams per 100 ml. of solution. Calculate also the milligrams of silver in one liter of saturated solution.

14. The solubility of strontium fluoride is 0.1193 g. per liter at 27°. Calculate its solubility product at 27°.

CHAPTER X

APPLICATION OF SOLUBILITY PRODUCT PRINCIPLE TO THE DETERMINATION OF CHLORIDE

202. Gravimetric Determination of Chlorine. General Considerations. — This determination is based on the precipitation of chloride ion as silver chloride by means of a solution of silver nitrate. For instance, in determining NaCl the reaction is

$$NaCl + AgNO_3 \rightarrow AgCl \downarrow + NaNO_3;$$
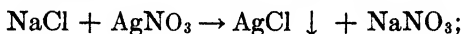
or writing the reaction ionically:

$$Cl^- + Ag^+ \rightarrow AgCl \downarrow .$$
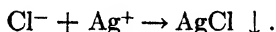
As silver ion forms insoluble salts with bromide, iodide and thiocyanate ions, these ions must be absent. Silver ion may also form insoluble compounds with cyanide, phosphate, and hydroxyl ions. The concentrations of these ions must be repressed by the addition of acid before adding the silver nitrate solution. It is the practice to render the solution about 0.002 M with respect to nitric acid. The volume of the solution from which precipitation is effected should be about 150–200 ml. and should not contain more chlorine than corresponds to 0.500 g. of silver chloride. The precipitation should be conducted at room temperature (18°–25°) by adding the precipitant dropwise. Only a slight excess of precipitant should be added beyond the calculated amount. After the precipitant is known to be in excess, the solution should be heated to about 90°–95° to coagulate the precipitate and thus facilitate subsequent filtration. In filtering, the use of a porous bottom crucible or Gooch crucible is much to be preferred over filter paper because, in the subsequent and necessary ignition of the paper, the resulting carbon reduces some of the silver chloride to metallic silver, and this, of course, must be converted back to the chloride, a procedure which is both time-consuming and bothersome.

Silver chloride is one of the most insoluble precipitates, its solubility in pure water at 25° being about 1.8 mg. per liter.

[252]

In washing this precipitate, however, the wash water should be slightly acidulated with nitric acid (0.01 M HNO_3 is a suitable washing solution) because, if the precipitate is washed with pure water, it tends to pass into the colloidal condition and so go through the filter. When the washing is complete, that is, when a fresh portion of the filtrate shows no test for silver ion, the nitric acid should be removed by washing the precipitate twice with distilled water. Silver chloride exhibits the phenomenon of becoming lightstruck. This phenomenon is evidenced by the precipitate's acquiring a purplish blue cast that varies in depth of color according to the intensity and duration of exposure. As this light action results in the formation of a sub-halide of silver with attendant loss of chlorine, silver chloride should always be protected from the influence of daylight as much as possible, and under no conditions ever be exposed to direct sunlight. Silver chloride is not very stable toward the action of heat; it may be dried safely at 110°–115°; at 451° it fuses, and, if heated much above this temperature, it begins to decompose. The treatment of the precipitate subsequent to washing depends on whether a Gooch crucible or a filter paper was used for filtration: if a Gooch crucible, the precipitate may be dried at 115° and weighed; if a filter paper, the procedure mentioned in § 204 must be followed.

If all due attention and care are paid to details, the precision which is attainable in the gravimetric determination of chlorides as silver chloride is 1 part per 1,000. In the hands of beginning students it is seldom that such a precision is obtained, their results ranging from 3 to 30 parts per 1,000 low.

Chlorine cannot be determined by this method in certain salts in which the chlorine exists more or less in the form of a complex ion in association with the metallic radical of the salt. Examples of such salts are mercuric chloride, stannous chloride, antimony chloride, platinic chloride and chromic chloride.

203. Exercise No. 7. Gravimetric Standardization of Approximately 0.1 M HCl by Precipitation as AgCl. Use of Gooch Crucible. — Make up 1 liter of approx. 0.1 M HCl.[1] Prepare

[1] If a standard approx. 0.1 M HCl has already been prepared as directed in § 164, it can be used here very advantageously.

two porcelain Gooch filters as directed in §32. Select two 300 ml. beakers, and measure accurately into each by means of a standard pipette or burette 25.00 ml. of the acid. Add about 150 ml. of water and 5 ml. of 0.1 M HNO_3. Protect the solution from strong daylight and add dropwise from a pipette and with constant stirring 0.1 M $AgNO_3$ until in slight excess (this excess should not exceed 5 ml.). After this addition but not before, heat the solution to about 90°–95° and stir until the precipitate coagulates, so that it will settle and leave a clear supernatant solution. Allow the precipitate to settle, and add to the clear solution one or two drops of the silver nitrate solution to make sure that an excess of precipitant is present. If there is no further precipitation, cover the beaker with a watch-glass, and set it aside for an hour or so to digest. After digestion, wash the precipitate of AgCl several times by decantation, and then transfer it to the Gooch crucible using a "policeman" (§ 26) if necessary, and continue washing with water which is slightly acidulated with nitric acid (0.01 M HNO_3 is a suitable washing solution) until the filtrate shows no test for silver. Now wash the precipitate twice with pure water to remove the nitric acid. Dry the crucible to constant weight (to 0.1 mg. for platinum, 0.2 mg. for porcelain) at 115° in an air bath or electric oven. Duplicate determinations should agree within 3 parts per 1,000. From the weight of AgCl found, calculate the value of the HCl solution.

204. Exercise No. 8. Gravimetric Standardization of Approximately 0.1 M HCl by Precipitation as AgCl. Use of Filter Paper. — Proceed exactly as described in the preceding exercise up to the point where digestion has been effected; from there on proceed as follows. Fit a $12\frac{1}{2}$ cm. ashless filter paper to its funnel and then moisten it thoroughly with water and tamp down the seams as directed in § 30, so that no precipitate can lodge back of the folds. The next operation is the filtration. Wash the precipitate of AgCl several times by decantation and then transfer it to the filter paper, using a "policeman" (§ 26) if necessary, and continue washing with water slightly acidulated with nitric acid (0.01 M HNO_3 is a suitable washing solution) until the filtrate shows no test for silver. Now wash the precipitate twice with pure water to remove the nitric acid. Now cover the funnel

with a filter paper, making it secure by crumpling its edges over the rim of the funnel so that they will engage the outer conical wall of the latter.   Next mark the funnel for identification, place it in a drying oven at 100°–110°, and leave it there until the precipitate and the filter paper are completely dry.   Now detach from the filter paper as much of the precipitate as is possible. To accomplish this, select a large watch-glass[2] about 6 inches in diameter and open the filter paper just above it in a place that is free from draughts.   By very gently rubbing the sides of the filter paper together, detach the greater portion of the precipitate from the paper and allow it to drop upon the watch-glass.   Care must be taken not to rub too hard as such rubbing will cause the paper itself to become abraded and fall into the main portion of the precipitate.   When as much of the precipitate has been detached as possible, the large watch-glass is covered with a smaller one, for the time being, and attention is directed to the filter paper with its small amount of remaining precipitate.   Now fold the paper carefully and place it inside of a weighed porcelain crucible; place the crucible on a triangle and ignite gently until the paper is charred, after which, conduct the ignition at a higher temperature until the carbon is all oxidized.   Then allow the crucible to cool, and moisten the ignited residue, consisting of' metallic silver, with 2–3 drops of 6 M HNO_3 and one drop of 2 M HCl, which may be advantageously added by dropping from a stirring rod.   After this, very cautiously heat the crucible (preferably in an air bath to avoid spattering) until the acids have been expelled.   Now transfer the main portion of the precipitate to the crucible by means of a camel's-hair brush and moisten in a similar manner with 2–3 drops of 6 M HNO_3 and one drop of 12 M HCl.   Expel the acids by very cautious heating (preferably in an air bath) and when the precipitate is white, slowly raise the temperature until the silver chloride just begins to fuse at the edges (about 450°).   Then cool the crucible in a desiccator and weigh.   Repeat the ignition (without the addition of acids however) and weigh again.   If the duplicate weighing does not agree with the first within 0.0003 g., carry out a third heating,

[2] If a watch-glass is not available, a similar sized piece of black glazed paper will answer the purpose.

cooling and weighing, and so on, until this concordance is obtained in two consecutive weighings. From the weight of AgCl found calculate the value of the hydrochloric acid solution.

205. Exercise No. 9. Gravimetric Determination of Chlorine in Sodium Chloride. — If the problem is to determine the percentage of chlorine in a sample of sodium chloride "as is," any ordinary grade of sodium chloride, such as table salt, will suffice. If, however, the problem is to see how nearly we can verify the theoretical percentage of chlorine in the chemical compound, sodium chloride, then the purity of our salt must be established beforehand. The most certain way of establishing this point is for the analyst to prepare the pure salt himself — a matter which is not very difficult. To prepare the pure salt, make up a saturated solution of a fairly good grade of sodium chloride (table salt will answer if there is nothing better at hand); then pass hydrogen chloride gas into this solution until a sufficient amount of sodium chloride precipitates; when this has happened, pour off the supernatant liquid and transfer the salt to a Gooch funnel which has an asbestos filter bed at its bottom; then wash the salt several times with water. Transfer a 5–10 g. portion of the salt to a large platinum dish and dry it to constant weight at 130°.[3] Now put the salt in a glass-stoppered bottle, and keep it in a desiccator. Sodium chloride is not very hygroscopic, so that unless the atmosphere is unusually damp it can be weighed out directly.

Procedure. Weigh out to the nearest tenth of a milligram about 0.250 g. sodium chloride, dissolve in 150 ml. water, acidulate the solution with 5 ml. 0.1 M HNO₃, and proceed thenceforth as directed either in Exercise No. 7, or (less preferably) in Exercise No. 8. Calculate the precentage of chlorine actually found.

206. Volumetric Determination of Chlorine in Soluble Chlorides. Mohr's Method.[4] General Remarks. — In this method

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[3] If it is not convenient to prepare purified sodium chloride as described and a good grade of "analyzed" sodium chloride is at hand, the purification may be dispensed with, but the heating to constant weight at 130° cannot be omitted, because the sample is very likely to contain some hydrochloric acid and some water, particularly the latter if the sample has been opened for any length of time.

[4] A. Classen, "Frederick Mohr's Lehrbuch der Chemisch-Analytischen Titrirmethode," 7th ed., p. 425, Fr. Vieweg u. Sohn, Braunschweig, 1896.

the solution of the soluble chloride is treated with a few milliliters of a dilute solution of potassium chromate to serve as indicator, and then titrated with standard silver nitrate solution. The end point is evidenced by the change in the color of the solution from a lemon yellow to a faint orange tint.

To show the application of theory to this method, let us consider the actual standardization of an approximately 0.1 M silver nitrate solution by means of sodium chloride. We weigh out a suitable amount of sodium chloride, say 0.1850 g., and then dissolve it in about 125 ml. of water; to this solution we add 3 ml. of 0.1 M potassium chromate solution, after which we are ready to begin the titration. The silver nitrate solution is added dropwise from a burette, and the sodium chloride solution stirred vigorously at the same time. The amount of silver nitrate equivalent to 0.1850 g. of sodium chloride can be found by solving for X in the proportion corresponding to the relationship

$$AgNO_3 \equiv NaCl$$
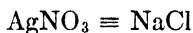
or

$$169.89 : 58.46 :: X : 0.1850$$

$$X = 0.5376 \text{ g. } AgNO_3.$$

When this weight of silver nitrate has been added, the concentration of silver ion in the solution will be equal to the concentration of chloride ion because of the fact that the total number of moles of silver in both phases will be equal to the total number of moles of chlorine, and an equal number of each has precipitated out as the solid phase. By virtue of this equality of concentration of the silver ion and the chloride ion at the stoichiometric point, the actual value of the two concentrations is easily derivable from the solubility product relationship for silver chloride. We have for this relationship

$$[Ag^+] [Cl^-] = 10^{-10}.$$

It follows that when the two concentrations are equal, their respective values must be

$$[Ag^+] = [Cl^-] = 10^{-5}.$$

Now as a result of adding 3 ml. of 0.1 M potassium chromate to the solution,

$$[CrO_4^-] = 2.0 \times 10^{-3}.$$

This chromate ion concentration is not sufficient to cause a precipitation of silver chromate at the stoichiometric point. To cause such a precipitation the concentration of chromate ion must exceed 2×10^{-2} in accordance with the solubility product relationship for silver chromate and the existent concentration of silver ion, *viz.*,

$$[Ag^+]^2[CrO_4^-] > 2 \times 10^{-12},$$

or putting in actual values

$$(10^{-5})^2 \times [CrO_4^-] > 2 \times 10^{-12}.$$

Whence,

$$[CrO_4^-] > 2 \times 10^{-2}.$$

The actual concentration which we have employed is 2.0×10^{-3} or one-tenth that demanded by theory. Two pertinent questions might now well be asked: (1), Why was not the theoretical amount of chromate used to give a precipitation of silver chromate when the concentration of silver ion became 10^{-5}? (2), How much more silver nitrate solution will have to be added beyond that point to give such a precipitation? The answer to the first question is a practical one. If the theoretical amount of indicator were used, the color of the solution would be such a deep orange that the appearance of the silver chromate would be almost undiscernible. To answer the second question, let us calculate the concentration which the silver ion must exceed in order to produce a precipitate of silver chromate. Solving for $[Ag^+]$ in the solubility product equation

$$[Ag^+]^2 \times 2.0 \times 10^{-3} = 2 \times 10^{-12},$$

we have

$$[Ag^+] = 3.2 \times 10^{-5}.$$

In increasing the silver ion concentration from 1×10^{-5} to 3.2×10^{-5}, by adding $AgNO_3$, further precipitation of $AgCl$ will take place. The maximum concentration of Ag^+ which can be used in precipitating Cl^- is somewhat less than 1×10^{-5} and the increase in $[Ag^+]$ necessary to go from the stoichiometric point to the point where Ag_2CrO_4 begins to precipitate is 2.2×10^{-5} moles per liter. The total silver ion concentration which must be furnished to the solution after reaching the stoichiometric point

is somewhat less than 3.2×10^{-5} moles per liter. If the volume of the solution is 150 ml. when Ag_2CrO_4 begins to precipitate, the volume of 0.1 M $AgNO_3$ needed is somewhat less than 0.048 ml. and if the total volume of $AgNO_3$ added is 25.00 ml. the error involved is less than 1.9 parts per 1,000.

So far we have said nothing about the hydrogen ion concentration of the solution which is being titrated because with sodium chloride, which is a salt that shows no hydrolysis, the pH of the solution would be around 5.8 and this is satisfactory. If, however, the solution were more acid than a pH of 4.0, the concentration of chromate ion would be so repressed by the displacement of the following equilibrium to the left

$$H_2CrO_4 \rightleftarrows HCrO_4^- \rightleftarrows CrO_4^-$$

$$\underset{\text{acid}}{\longleftarrow} \qquad\qquad \underset{\text{alkaline}}{\longrightarrow}$$
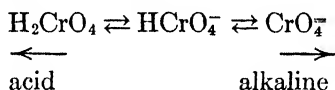
that, as a result, the solubility product of the silver chromate would not be exceeded and we would fail to get an end point. If, on the other hand, the solution were much more alkaline than a pH of 7.3, the concentration of hydroxyl ion would be such that silver oxide might be precipitated, owing to the solubility product of silver hydroxide ($K_{AgOH} = 2.3 \times 10^{-8}$) being locally exceeded

$$[Ag^+][OH^-] > K_{AgOH}.$$

These considerations always necessitate careful attention to the establishment of the proper concentration of hydrogen ion in Mohr's method, namely, a concentration lying between a pH of 4.0 and 7.0. If this method is used to determine chloride in a sample of hydrochloric acid, the pH can be brought within the range mentioned by adding either ammonium hydroxide solution or powdered calcite (natural calcium carbonate). The calcite must, of course, be chloride free. If the solution being titrated is more alkaline than corresponds to a pH of 7.3, it can be brought within the desired range by titrating with 0.1 M nitric acid.

207. Exercise No. 10. Volumetric Standardization of Approximately 0.1 M AgNO₃ Solution by Means of Sodium Chloride (Application of Mohr's Method). — Prepare about 500 ml. of approximately 0.1 M silver nitrate solution and about 50 ml. of

0.1 M potassium chromate solution. Standardize the silver nitrate solution as follows: Pulverize about 1 g. of pure fused sodium chloride, spread it in a thin layer on a watch-glass and dry it at 110°–120° for an hour.   Select three 250 ml. casseroles[5] and weigh out accurately, to the nearest tenth of a milligram, varying amounts of the sodium chloride, say, about 0.160 g., 0.170 g., and 0.180 g., and transfer them to each casserole, respectively, the casseroles being marked I, II, III for identification.   Add to each casserole 125 ml. of water and 3 ml. 0.1 M K_2CrO_4 solution and then titrate with the silver nitrate solution, which should be added slowly with attendant stirring of the solution in the casserole. When the silver nitrate forms a precipitate of Ag_2CrO_4 which changes slowly into AgCl as the mixture is being stirred, the end point is not far away,[6] and the further addition of the $AgNO_3$ solution must be made with caution.   The end point of the titration is marked by the transition in color from a lemon yellow to a faint orange tint which does not disappear on stirring.   This change of color can only be judged satisfactorily by having at hand for comparison another casserole containing a similar volume of water, the same amount of indicator, and about 0.100 to 0.200 g. NaCl, to all of which has been added 10–15 ml. of the silver nitrate solution. These quantities and conditions serve to establish the lemon yellow color in regard to which the end point must appear to be a faint orange tint.   As the end point is difficult to recognize, it is a good plan at first for students to get the assistance of the instructor.   The duplicate and triplicate titrations are run in the same manner.   The individual results of each titration are then calculated, and, if the average deviation of the series is not more than 2 parts per 1,000, the average of the determinations is taken as the value of the silver nitrate solution.   If the average deviation is greater than that mentioned, further titrations must be made until, excluding doubtful determinations (§ 58), the average deviation is brought down to the desired figure.   If, after

[5] It will be found preferable to employ casseroles rather than beakers as it is easier to judge the end point when casseroles are used.

[6] Very often at this juncture, but not always, the precipitated AgCl will coagulate; it is not advisable, however, to count on this coagulation as an index of the approaching end point.

repeated trial, a student finds it impossible to obtain an average deviation better than 7–10 parts per 1,000, it is very likely that he is troubled with color blindness.

To illustrate the method of calculating the molarity of the $AgNO_3$ solution, let us suppose that as the average of three titrations we find that

$$1 \text{ ml. } AgNO_3 \equiv 0.005850 \text{ g. NaCl.}$$

Since

$$AgNO_3 \equiv NaCl,$$
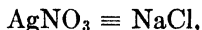
then

$$1,000 \text{ ml. } M \text{ } AgNO_3 \equiv 58.46 \text{ g. NaCl,}$$

and

$$1 \text{ ml. } M \text{ } AgNO_3 \equiv 0.05846 \text{ g. NaCl.}$$

Dividing the NaCl value of the solution being standardized by that of a molar solution, we obtain the molarity. Thus,

$$\frac{0.005850}{0.05846} = 0.1001 \text{ } M.$$

The results may be conveniently tabulated in the notebook and on the report card in a manner similar to that suggested for the standardization of HCl given in § 164.

208. Exercise No. 11. Volumetric Standardization of Approximately 0.1 M HCl Solution[7] by Means of Standard Silver Nitrate Solution (Mohr's Method). — Use the standard silver nitrate solution prepared above and run the determinations in triplicate. Measure accurately from a burette into a casserole about 30 ml. of the HCl solution and dilute with 100 ml. distilled water; add 1–2 drops of methyl orange solution and neutralize the acid with dilute NH_4OH until the end point of methyl orange is just reached.[8] To this neutralized solution add 3 ml. 0.1 M potassium chromate solution and titrate with the standard silver nitrate solution as described in the preceding exercise. Calculate the value of the acid and compare the value with those obtained by the procedures of §§ 203, 204. The average deviation for this determination should not be more than 2 parts per 1,000.

[7] If a standard HCl solution has already been prepared for Exercise No. 3, § 174, or Exercise No. 7, § 203, it can be used here.

[8] The presence of the methyl orange does not seem to interfere in any way with the precision of this determination.

209. Exercise No. 12.   Determination of Potassium Chloride in a Mixture of Sodium Carbonate and Potassium Chloride (Mohr's Method). — Weigh out into a casserole such a quantity of sample as will require about 30 ml. of 0.1 M silver nitrate solution. This presupposes an approximate knowledge of the composition of the sample. If the analyst does not possess such knowledge, he should first run a rough preliminary determination in order to obtain it. Having weighed out the appropriate amount of sample,[9] dissolve it in 100 ml. of distilled water, add 1-2 drops of methyl orange solution, and neutralize the alkaline solution with 0.1 M nitric acid solution until the methyl orange end point is reached. To the neutralized solution add 3 ml. 0.1 M potassium chromate solution and titrate with standard silver nitrate solution as described in § 206. The percentage of potassium chloride in the sample should be reported on the *dry basis* (§ 5); this will necessitate a separate determination of the moisture. To make this determination, clean a porcelain crucible and dry it in the oven at 110°–115° for an hour. After allowing it to cool in a desiccator, weigh it. Transfer 2–3 g. of sample to the crucible, obtaining the exact weight; put the crucible and its contents in the oven at 110°–115° and dry for 4 hours or overnight; allow to cool in desiccator and weigh. Repeat the drying, cooling and weighing until constant weight is obtained (§ 38). The loss in weight is taken as representing the amount of moisture.

To illustrate the calculation of results, let us suppose that a sample containing 2.41% moisture and weighing 1.1022 g. required 30.20 ml. of 0.1002 M $AgNO_3$. Since

$$AgNO_3 \equiv KCl,$$
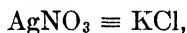
and   1,000 ml. M $AgNO_3 \equiv 74.56$ g. KCl,

it follows that

$$30.20 \text{ ml. of } 0.1002 \ M \ AgNO_3 \equiv \frac{74.56 \times 30.20 \times 0.1002}{1,000} \text{ g. KCl}$$

$$30.20 \text{ ml. } 0.1002 \ M \ AgNO_3 \equiv 0.2256 \text{ g. KCl,}$$

and $\dfrac{0.2256 \times 100}{(1.00-0.0241)\ 1.1022} = 20.98\%$ KCl on dry basis.

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[9] Whenever a sample of powdered material is being weighed out, it should be critically examined as to its homogeneity. If there is any evidence of non-homogeneity, such as large or strange particles or unevenness of color, etc., the acceptance of the sample for analysis is open to severe criticism.

Another method of obtaining the weight of KCl in the sample would be to convert the NaCl value of the silver nitrate solution to the corresponding KCl value by means of the appropriate chemical factor and then to multiply the number of milliliters of silver nitrate used by the KCl value.

The results of this determination may be conveniently tabulated in a manner similar to that suggested for the determination of Na_2CO_3 given in § 177.

210. Adsorption Indicators for Chloride Determination.[10]— Some of the silver chloride produced in the titration of chloride ion by means of silver nitrate may form a colloidal solution. When an excess of chloride ion is present, the colloid particles have a negative charge due to the adsorption of chloride ion. When, however, the stoichiometric point has been reached, further addition of silver nitrate produces an excess of silver ions. Under these conditions the colloid particles acquire a positive charge, due to adsorption of silver ions. Negative ions present in the solution may be adsorbed by these positively charged particles. A few drops of a solution of the sodium salt of dichlorfluorescein added at the beginning of the titration will furnish to the solution the negative dichlorfluoresceinate ion. When these ions are adsorbed by the positively charged colloid particles, the surface of the particles acquires a purplish color. The appearance of this purplish color, just after the stoichiometric point has been reached, is taken as the end point of the titration. The indicator used is the salt of a weak acid, and, when used in solutions more acid than a pH of 4, the dichlorfluoresceinate ion is repressed sufficiently to prevent it from giving a satisfactory end point.

Sodium fluoresceinate may also be used as an indicator. It is the salt of an even weaker acid than is sodium dichlorfluoresceinate and, consequently, it must be used in solutions which are less acid. Unsatisfactory results are obtained when the pH is more acid than 6.5.

211. Exercise No. 13. Determination of Potassium Chloride by Adsorption Indicator Method. — Weigh out an amount of sample requiring about 35 ml. of 0.1 M silver nitrate solution.

[10] Kolthoff, Lauer, and Sunde, *J. Am. Chem. Soc.*, **51**, 3273 (1929).

Dissolve it in about 50 ml. of solution. Add about 8 drops of a 0.1% solution of sodium dichlorfluoresceinate. Titrate the solution to the end point with vigorous agitation. A color change from a yellowish green to purple marks the end point. The error involved in titrating beyond the stoichiometric point to produce the end point is generally small enough to be neglected.

212. Indirect Determinations.[11]— Indirect determinations are based upon the principle that if we have a mixture of two salts having the same acid or basic radical, it is possible to calculate the weight of each salt from the weights of the mixture and of the common radical. Thus, if we start with a known weight of a mixture of potassium and sodium chlorides and determine the weight of chlorine, then we can calculate the respective weights of the potassium chloride and the sodium chloride. The example that we have chosen, namely, the case where we have a mixture of potassium and sodium chlorides, has been purposely selected because it represents not only the best case which can be handled by the method of indirect determinations but also the most frequent case which is met with in practice.

Let us suppose that the weight of the mixed potassium and sodium chlorides taken for analysis is 0.5324 g. and that the weight of the chlorine obtained from this sample is 0.2838 g.; and that we are to find the respective weights of the two chlorides. To do this we proceed as follows:

Let

$$x = \text{grams KCl in mixture}$$

$$y = \quad\text{``}\quad \text{NaCl ``} \quad\text{``} \quad .$$

Then,

$$\frac{35.46\,x}{74.56} = \text{grams Cl in KCl}$$

$$\frac{35.46\,y}{58.46} = \quad\text{``}\quad\text{``}\quad\text{``} \text{ NaCl,}$$

[11] For extended information on the subject of Indirect Determinations, consult the following: Mellor, p. 229 of reference given in § 11; J. Fages y Virgili, "Die indirekten Methoden der analytischen Chemie," Ferdinand Enke, Stuttgart, 1911; W. M. Dehn, "Analysis of Mixtures of Halogen Acids," *J. Am. Chem. Soc.*, **31**, 1273 (1910).

and we have accordingly,

$$x + y = 0.5324$$

$$\frac{35.46\,x}{74.56} + \frac{35.46\,y}{58.46} = 0.2838;$$

which upon solving, gives

$$x = 0.2992$$

$$y = 0.2332.$$

A variation of the foregoing scheme is to use one unknown quantity, but this scheme, while simplifying the algebra of the problem, complicates the arithmetic, as can easily be verified by working through the following solution:

Let

$$x = \text{grams KCl in mixture.}$$

Then,

$$0.5324 - x = \text{grams NaCl in mixture}$$

and

$$\frac{35.46\,x}{74.56} = \text{grams Cl in KCl}$$

$$\frac{35.46}{58.46}\,(0.5324 - x) = \text{grams Cl in NaCl.}$$

Whence

$$\frac{35.46\,x}{74.56} + \frac{35.46}{58.46}\,(0.5324 - x) = 0.2838$$

$$0.4756\,x + 0.3230 - 0.6066\,x = 0.2838$$

$$x = 0.2992$$

$$(0.5324 - x) = 0.2332.$$

A third scheme, which in the authors' experience is far superior to either of the two preceding schemes, is this: Instead of letting x and y represent the grams of KCl and NaCl in the mixture, let them represent the number of moles of KCl and NaCl. This method leads to equations similar in form to those just considered

but often easier to solve because the coefficients are not fractional, thus,

Let $\qquad\qquad\qquad x =$ moles KCl in mixture

$\qquad\qquad\qquad\qquad y =$ "   NaCl "   "   .

Then $\qquad\qquad\quad x + y =$ moles Cl in mixture

and $\qquad\qquad\quad 74.56\,x =$ grams KCl

$\qquad\qquad\qquad 58.46\,y =$ "   NaCl

$\qquad\qquad 35.46\,(x + y) =$ grams Cl;

whence $\qquad\quad 74.56\,x + 58.46\,y = 0.5324$

$\qquad\qquad 35.46\,(x + y) = 0.2838;$

which upon solving gives,

$$x = 0.004008$$

$$y = 0.003995$$

and $\qquad 74.56\,x = 0.2992 =$ weight of KCl in grams

$\qquad\quad 58.46\,y = 0.2332 =$ "   " NaCl "   "   .

The percentages of NaCl and KCl in a sample consisting entirely of a mixture of these two chlorides can be obtained by the following alternative method:

1. The chloride in the sample is precipitated by Ag^+ and the weight of AgCl formed is determined.

2. The grams of AgCl per gram of sample is calculated.

3. The per cent of NaCl is obtained from the curve of Figure 49.
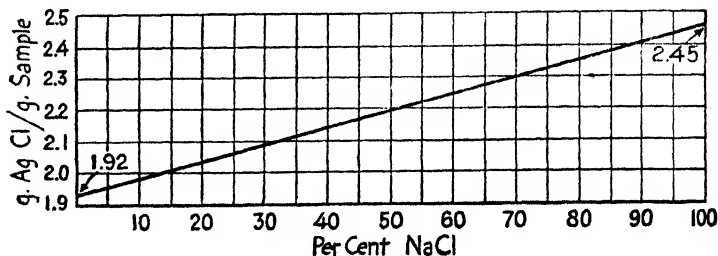
Fig. 49

Relationship between Grams of AgCl per Gram of Sample, and Per Cent of NaCl in Sample

4. The per cent of KCl is obtained by subtracting the per cent of NaCl from 100.

To illustrate the method of construction of Figure 49, let us suppose the weight of AgCl per gram of sample was found to be 2.45 g.   Then

$$\frac{\text{AgCl}}{\text{NaCl}} = \frac{143.34}{58.46} = \frac{2.45}{X}$$

and

$$X = 1.00 \text{ g.}$$

We see that in this case the entire sample consists of NaCl. If the weight of AgCl per gram of sample had been 1.92 g., then

$$\frac{\text{AgCl}}{\text{KCl}} = \frac{143.34}{74.56} = \frac{1.92}{X}$$

and

$$X = 1.00 \text{ g.}$$

In this case the sample would consist entirely of KCl.   From the straight line connecting 2.45 and 1.92, intermediate percentages of NaCl and KCl can be obtained.   Thus, 2.13 g. AgCl per gram of sample corresponds to 40.0% NaCl and 60.0% KCl.

213. Limitations of Indirect Determinations.[12]— The principle of Indirect Determinations cannot be applied to all pairs of salts, as a study of the following considerations will show.

Let the two salts have the formula MA and NA, and let their combined weight in a mixture solely of the two be w, while the weight of the common constituent A is u.
Let

$$p = \text{number of moles of } MA \text{ in the mixture}$$

$$q = \text{``} \quad \text{``} \quad \text{``} \quad \text{`` } NA \text{ `` `` } \quad \text{``} \quad .$$

Obviously,

$$M + A = \text{molar weight of } MA$$

$$N + A = \text{`` } \quad \text{`` } \quad \text{`` } NA.$$

Then

$$p(M + A) = \text{grams of } MA \text{ in the mixture}$$

$$q(N + A) = \text{`` `` } NA \text{ `` `` } \quad \text{``}$$

$$pA + qA = \text{`` `` } A \text{ `` `` } \quad \text{``}$$

[12] The subject matter of this paragraph is adapted largely from Mellor, p. 229 of reference given in § 11.

and we have accordingly,

$$pA + qA = u$$

$$p(M + A) + q(N + A) = w$$

which upon being solved, give

$$p = \frac{wA - u(A + N)}{A(M - N)}; \quad q = \frac{wA - u(A + M)}{A(N - M)}.$$

For our purposes, however, we require the respective weights of M and N, namely, the quantities pM and qN. These weights are seen to be:

$$\text{grams of } M = pM = \frac{M}{A} \frac{wA - u\,(A + N)}{(M - N)},$$

$$\text{grams of } N = qN = \frac{N}{A} \frac{wA - u\,(A + M)}{(N - M)}.$$

Since the weight of the mixture itself is w, we have as the percentage of M in the mixture

$$\text{percentage of } M = \frac{100M}{A\,(M - N)} \times \frac{wA - u\,(A + N)}{w}$$

and a similar expression for the percentage of N.

We see at a glance that the first factor of the right-hand member is constant for a particular pair of salts, and that the greater the value of this factor, the greater the influence of errors in the determination of u and w on the final result. With a mixture of potassium and sodium chlorides, the factor is nearly 7; with magnesium and calcium sulfates, 2.6; and with nickel and cobalt sulfates, 246. Thus, so far as the calculations themselves are concerned, it is easy to see that the indirect method is applicable to a mixture of magnesium and calcium sulfates with more reliability than it is to a mixture of potassium and sodium chlorides, while in the case of nickel and cobalt, sulfates, the method is valueless because the errors in the determination are multiplied so enormously. Hence, other things being equal, the calculated values of M and N will be the more accurate,

1. The smaller the numerical values of the equivalent weights of the constituents M and N,

2. The greater the difference between the equivalent weights of the constituents M and N,

3. The greater the equivalent weight of the single constituent A.

In general, it is to be remarked that indirect methods of analysis are to be avoided.

214. Examples.

1. In standardizing an approximately 0.1 M silver nitrate solution for use in Mohr's method, the following results were obtained by a student:

g. NaCl used	*ml. silver nitrate solution required*
0.2008	32.34
.2239	35.99
.2551	41.06

What was the molarity of the silver nitrate solution?   Ans.   0.1063 M.

2. How many g. of silver nitrate per liter will give a solution equivalent to 1 mg. of chlorine per milliliter?   Ans.   4.79 g.

3. What molarity of silver nitrate solution will be required in order that 1 ml. of the solution shall represent 1% of potassium chloride in a sample when 0.500 g. of sample is taken for analysis?   Ans.   0.06706 M.

4. How many ml. of 0.2 M HCl must be taken in order to yield a precipitate of 0.500 g. AgCl?   Ans.   17.44 ml.

5. A mixture of pure NaCl and KCl weighing 0.1150 g. gave a precipitate of AgCl weighing 0.2531 g.   Calculate the per cent of NaCl and KCl in the mixture.

6. From 0.5324 g. of a mixture of potassium chloride and sodium chloride, 1.1472 g. of silver chloride were obtained.   What were the weights of potassium and of sodium in the mixture?
Ans.   0.1567 g. K   0.0920 g. Na.

7. A mixture of NaCl and KCl was treated with sulfuric acid, evaporated to dryness and ignited at red heat.   The weight of the residue was 0.8066 g.   This was dissolved in water and treated with an excess of BaCl$_2$ after slightly acidulating the solution with hydrochloric acid. The precipitate was filtered off on a Gooch crucible, dried, and found to weigh 1.1670 g.   What were the weights of NaCl and KCl in the original mixture?   Ans.   NaCl = 0.2345 g.   KCl = 0.4464 g.

8. From 0.5170 g. of a mixture of Na$_2$CO$_3$ and NaHCO$_3$, 0.2420 g. of CO$_2$ were obtained.   What were the weights of each carbonate?
Ans.   0.2650 g. Na$_2$CO$_3$ 0.2520 g. NaHCO$_3$.

9. A 0.7530 g. sample of a nickel-silver alloy was dissolved in nitric acid, neutralized and treated with 50.00 ml. of 0.1120 M NaCl solution. The mixture was diluted to 250.0 ml. and filtered.   The excess chloride in 200.0 ml. of the filtrate required on titration 30.15 ml. of 0.1015 M AgNO$_3$ solution.   Calculate the approximate per cent of Ag in the alloy.   Point out an important source of error inherent in the method.

CHAPTER XI

APPLICATION OF SOLUBILITY PRODUCT PRINCIPLE TO THE DETERMINATION OF SILICON, SULFUR AND PHOSPHORUS
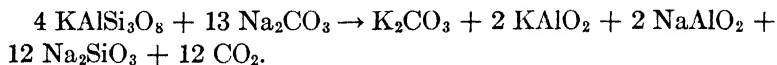
215. General Considerations. — In proceeding to show further applications of the solubility product principle to the determination of some of the more common elements, it will be advantageous to select not only simple laboratory exercises for each element but to supplement such simple exercises by additional determinations which will involve the difficulty of one or more prior separations as an essential preliminary to the determination of the element or constituent desired.

It will be found in a great number of various determinations that the very first separation that must be effected before further work can be done on the desired constituent is the separation of silicon, so that the logical thing to do at this juncture is to familiarize ourselves somewhat in detail with this problem.

216. Prior Removal and Determination of Silicon. — The frequency of the separation arises from two facts: First, that silicon (as silicic acid) is dragged down to a surprising degree by practically every insoluble precipitate; second, that silicon is almost invariably associated with those elements which have to be determined by means of their insoluble precipitates. This is particularly true with such frequently occurring elements as phosphorus, aluminum, calcium, and magnesium, which engage so large a part of an analyst's time because of their occurrence in the important classes of substances represented by iron and steel products, ferrous alloys, rocks, clays, soils, slags and cements.

The forms in which the element silicon may occur are as follows: As free silicon, or in combination as a silicide, or as a silicate. In the first two cases it must first be oxidized to silicic acid by means of nitric acid; in the case of silicates, we encounter two kinds of compounds, those soluble in mineral acid and those insoluble. The latter must be rendered soluble by fusion with

sodium carbonate.   Thus, to take the case of the insoluble silicate rock, feldspar, we have as a typical illustration:

$$4 \text{ KAlSi}_3\text{O}_8 + 13 \text{ Na}_2\text{CO}_3 \rightarrow \text{K}_2\text{CO}_3 + 2 \text{ KAlO}_2 + 2 \text{ NaAlO}_2 + 12 \text{ Na}_2\text{SiO}_3 + 12 \text{ CO}_2.$$

All soluble silicates upon treatment with mineral acid decompose according to the scheme,

$$\text{Na}_2\text{SiO}_3 + 2 \text{ HCl} \rightarrow 2 \text{ NaCl} + \text{H}_2\text{SiO}_3;$$
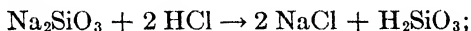
but, generally speaking, we do not get meta-silicic acid alone as represented in the reaction, but a mixture of ortho, meta, tri- and di-silicic acids in varying proportions according to conditions of concentration, acidity, temperature, etc.   These various forms of silicic acid have a descending order of solubilities in the succession given, namely,

ortho-silicic acid H_4SiO_4 or $SiO_2 \cdot 2 H_2O$, soluble,
meta-   "   " H_2SiO_3 " $SiO_2 \cdot H_2O$, partially soluble,
tri-   "   " $H_4Si_3O_8$ " $3 SiO_2 \cdot 2 H_2O$,   "   "
di-   "   " $H_2Si_2O_5$ " $2 SiO_2 \cdot H_2O$, nearly insoluble.

The separation of silicon, in whatever form it may be found in the sample submitted, is based upon the procedure of getting it in the form of free silicic acid, then evaporating the silicic acid to dryness and dehydrating it at any convenient temperature between 105° and 120° in order to convert it to $SiO_2 \cdot \frac{1}{2}H_2O$ which is soluble only to a slight extent.   The dried residue is then digested with a few milliliters of 12 M HCl for a few minutes in order to dissolve the accompanying soluble salts, after which a little water is added and the dehydrated silicic acid is filtered off. This dehydrated silicic acid will be contaminated more or less by salts of the bivalent and trivalent elements of the iron group, if these latter are present.   The filtrate will contain about 2–3% of the silicic acid in soluble form, and, if it is necessary to separate this also, the filtrate is evaporated to dryness and the residue is dehydrated as before.

Upon evaporation to dryness and dehydration at 105°–120° the ortho, meta, and tri-silicic acids are converted to the di-silicic acid which is soluble only to the extent of about 2%, that is to say,

if the silicic acid being dehydrated contained the equivalent of 0.100 g. SiO_2, only about 2 mg. (figured as SiO_2) would go back into solution when the soluble salts accompanying it were dissolved. If it is necessary to get rid of the soluble portion which goes back into solution, then the dehydrated silicic acid must be filtered off, and the filtrate containing the soluble silicic acid again evaporated to dryness and dehydrated; the newly dehydrated portion, however, like the first portion, will be soluble to the extent of 2–3%. For precise work when dealing with amounts of silica much over 30 mg., two or three dehydrations, *always with intervening filtration,* will be necessary according to the quantity of silica present.

If it is required not only to remove silicon from the solution, but also to determine it as well, the filters containing the residues undissolved by hydrochloric acid are ignited to constant weight in a platinum crucible. The silicon dioxide formed by this procedure is generally contaminated. In order to obtain the weight of SiO_2 present, H_2SO_4 is added, followed by concentrated HF. The SiO_2 is decomposed, yielding volatile SiF_4, as shown in the following reaction:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O.$$
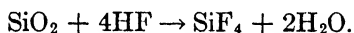
By evaporating to dryness and igniting to constant weight, the loss in weight due to the removal of SiO_2 can be determined and the per cent of SiO_2 in the original sample can be calculated. The H_2SO_4 must be present during treatment with HF so that any titanium present will not be liberated as TiF_4 but will be retained in the residue as TiO_2, and also in order that other oxides present in the residue will remain as such and not be converted to fluorides. The details of this determination are given in § 230.

217. Determination of Sulfur. — The method that is most generally used for the determination of sulfur is the gravimetric method, which is based upon the procedure of getting the sulfur into solution in the form of sulfate ion and then precipitating it as barium sulfate by means of a solution of barium chloride. The reaction taking place is:

$$SO_4^- + Ba^{++} \rightarrow BaSO_4 \downarrow .$$
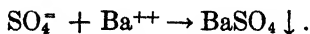
The reason for the wide use of this method is to be found in the fact that sulfur occurs very often in the form of sulfate, and that when it does occur in any of its other forms, namely, as free sulfur, sulfide, sulfite, etc., these are readily oxidizable to sulfate. In the precipitation of sulfate ion as barium sulfate it is to be noted that carbonate ion, phosphate ion, or chromate ion must be absent or their concentrations sufficiently diminished by regulation of the acidity of the solution so that they will not be precipitated (§ 126). It is the practice, therefore, when precipitating barium sulfate to have the solution slightly acid by making it about 0.1 M with respect to HCl. Barium sulfate is one of the most insoluble precipitates, its solubility being about 2 mg. per liter at 20°. However, it exhibits to a remarkable degree the phenomenon of co-precipitation as already mentioned in § 190, dragging down barium chloride, sodium and potassium nitrates, ferric sulfate and many other soluble salts so that it is really a difficult matter to obtain a pure precipitate of barium sulfate. The extent of co-precipitation depends to a considerable extent on the following factors:

1. Concentrations of contaminants.
2. Concentration of sulfate solution.
3. Concentration of hydrogen ion.
4. Rate of addition of barium chloride.
5. Rate of stirring.
6. Temperature of precipitation.
7. Temperature and duration of digestion.

When $SO_4^=$ is practically completely precipitated by an equivalent amount of Ba^{++} and in addition contaminating ions such as K^+, Ba^{++}, NO_3^- and Cl^- co-precipitate, the precipitate will be heavier than the theoretical value. This often occurs when the concentrations of hydrogen ion and alkali chloride are small. Thompson [1] studied the effects of variations in nitrate concentration, rate of addition of barium chloride and excess of barium chloride used, by determining the extent that $BaSO_4$ precipitates exceeded the theoretical weight when precipitated from un-

[1] W. S. Thompson, "A Study of Factors Influencing the Quantitative Determination of Sulfate as Barium Sulfate," *Ind. Eng. Chem., Anal. Ed.* **11,** 206 (1939).

acidified 0.01 M K_2SO_4 solutions at 95°–100°. These precipitates were digested at 25° for 24 hours and heated to constant weight at 110°–120°. The results are presented by means of the curves of Figure 50.
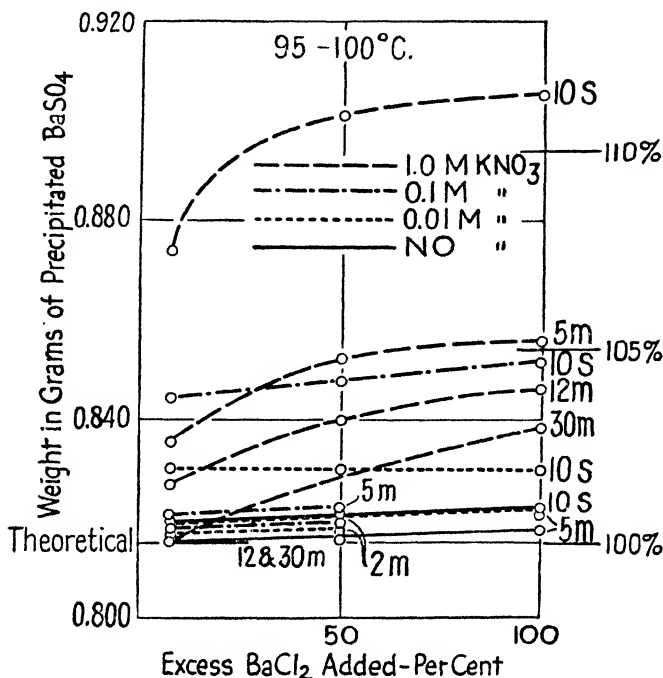

Fig. 50

Weight of Unignited Precipitate, in Per Cent of Theoretical Value

Obtained by adding 5, 50 and 100 per cent excess of 0.05 M $BaCl_2$ to 350 ml. of unacidified 0.01 M K_2SO_4, 0.00 M, 0.01 M, 0.1 M and 1.0 M with respect to KNO_3, where the first 105 per cent of $BaCl_2$ was added in 10 seconds, 5, 12 and 30 minutes. The temperature at start of precipitation was 95°–110°. The precipitates were digested 24 hours at 25°.

It is seen from these results that, in general, the excess weight of the precipitate increases with the concentration of nitrate, with the rate of addition of barium chloride, and with the excess of barium chloride used. However, it is clear that when the concentration of nitrate is 0.01 M or less and the time of addition of barium chloride is 12 minutes or more, 50% excess of barium

chloride yields a precipitate which is only very slightly heavier than the theoretical value. When lower temperatures are maintained during precipitation, the excess weight of the precipitate may be considerable, even when the barium chloride is added very slowly to solutions containing very low concentrations of potassium nitrate.

The effect of variation in hydrogen ion concentration for precipitations made from $0.01\ M$ K_2SO_4 solutions containing different concentrations of potassium nitrate, when digestion is carried out at 25° for 24 hours, is shown by Thompson's results
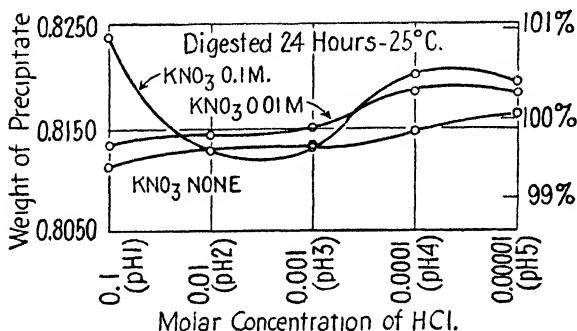
Fig. 51

Weight of Unignited Precipitate

Obtained by adding $0.05\ M$ BaCl$_2$ 5 per cent excess in 5 minutes to $0.01\ M$ K$_2$SO$_4$ at 95°–100° containing varying concentrations of HCl and KNO$_3$.

presented by means of the curves of Figure 51. It is seen from these results that when the concentration of potassium nitrate is $0.01\ M$ or less, an increase in the hydrogen ion concentration counteracts, to some extent, the tendency of the nitrate to produce a precipitate heavier than the theoretical value. For approximately $0.01\ M$ nitrate solutions, a pH between 1 and 3 is desirable. For other concentrations of nitrate, the pH should be between 2 and 3. The production of a precipitate which is lighter than the theoretical value may be due to co-precipitation of H^+ and K^+ in place of some Ba^{++}. These ions weigh less than equivalent quantities of Ba^{++}, and tend to give low results. For the same reason, the contamination of the precipitate by Fe^{+++}

may also lead to low results.   To diminish the error due to Fe^{+++}, the iron may be removed as $Fe(OH)_3$ precipitate by adding the solution to NH_4OH as described in § 230, or it may be reduced to ferrous ion by the addition of metallic zinc or of hydroxylamine.

Barium sulfate is fairly stable on ignition and can be heated to 1,000° without decomposition, provided reducing substances are not present.   In the presence of carbon, barium sulfate is reduced to the sulfide at temperatures around 500° to 600° according to the reaction,

$$BaSO_4 + 2\ C \rightarrow BaS + 2\ CO_2.$$
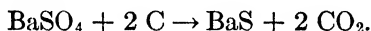
For this reason the use of filter paper in the filtration of barium sulfate is objectionable because, upon the subsequent ignition, the carbon which results from the charring of the paper reduces some of the sulfate to sulfide, and this latter must be reconverted to the sulfate.   It is often erroneously stated that treatment with a few drops of concentrated nitric acid will effect the oxidation of the sulfide to the sulfate according to the scheme,

$$3\ BaS + 8\ HNO_3 \rightarrow 3\ BaSO_4 + 8\ NO + 4\ H_2O.$$

In point of fact, however, treatment with nitric acid transposes the sulfide to nitrate and this latter upon ignition at temperatures of 500°–800° goes over to a mixture of the oxide and peroxide, thus,

$$BaS + 2\ HNO_3 \rightarrow Ba(NO_3)_2 + H_2S$$

$$4\ Ba(NO_3)_2 + \Delta \rightarrow 2\ BaO_2 + 2\ BaO + 8\ NO_2 + O_2.$$
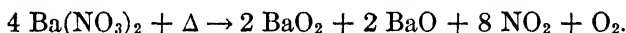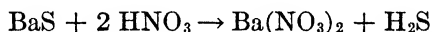
The remedy for taking care of any sulfide that may be formed is to treat the precipitate with one or two drops of 18 M sulfuric acid.   The reaction taking place is as follows:

$$BaS + H_2SO_4 \rightarrow BaSO_4 + H_2S.$$

The excess sulfuric acid is removed by heating to 300° in an air bath (§ 20).

The following duplicate determinations, made in the laboratory of one of the authors [2] show the mistake of trying to use nitric acid to convert the sulfide to sulfate:

[2] H. A. Fales.

	A	*B*
Weight of BaSO₄ precipitate after burning off filter paper and igniting to constant weight	0.3426 g.	0.3433 g.
Weight after treating with 4 drops 16 *M* HNO₃ and re-igniting	0.3290 g	0.3305 g.
Weight after treating with 4 drops 18 *M* H₂SO₄ and re-igniting	0.3447 g	0.3454 g.

Since serious errors may occur as a result of ignition, especially when the amount of nitrate contamination is large, it is preferable to collect the precipitate in a porous bottom crucible or a Gooch crucible and to dry it to constant weight at 110°–120°.

218. Summary of Conditions for the Determination of Sulfur. — The amount of sample to be weighed out should contain an amount of sulfate not greater than corresponds to about 0.850 g. BaSO₄. The volume of solution should be about 300–350 ml. and should be acidulated with 1 ml. of 1 *M* HCl per 100 ml. of solution to give a pH between 2 and 3. It is desirable that only salts of the alkali group be present and that nitrates and chlorates be absent. Satisfactory results can be obtained in the presence of nitrates, provided due care is exercised in establishing the proper conditions as previously explained. When iron is present, as in the analysis of steel, a pH between 1 and 2 should be used. The temperature of precipitation should be 90°–95°, and 0.05 *M* barium chloride solution should be added dropwise over a period of 30 minutes with constant stirring. A 50% excess of barium chloride may be used. The precipitate should be allowed to digest for 24 hours at 25°. For amounts of precipitate under 5 mg., this time should be extended to 48 hours. The precipitate should be filtered through a Gooch crucible, or porous bottom crucible, and dried at 110°–120° for 12 to 18 hours.

Precision.—While concordant checks to a precision of 1 part per 1,000 can be obtained for duplicate determinations of sulfates, it is almost certain that these will be attended with a constant error of at least 2 parts per 1,000 (see § 53), and if salts which are adsorbed are present, this constant error may reach 30 parts per 1,000.

219. Exercise No. 14. Determination of Sulfate in a Mixture of Soluble Chlorides, Sulfates, Carbonates, and Nitrates.[3]— Weigh out an amount of sample which will furnish about 0.500 g. $BaSO_4$ and transfer it to a beaker, dissolve it in 250 ml. of water, add 6 ml. of 3 M HCl, and heat to near the boiling point. Add dropwise with stirring from a burette a solution of 0.05 M $BaCl_2$ to 50% excess. Cover the beaker with a watch-glass and set it aside for 24 hours so that the precipitate can digest; in the meantime prepare a Gooch crucible or porous bottom crucible. After digestion, and before filtration of the precipitate, add to the clear solution a few drops of the $BaCl_2$ solution, and if more precipitate forms, continue the addition of the barium chloride until the barium ion is in about 50% excess. Without disturbing the precipitate, decant the clear solution through the filtering crucible. Add about 50 ml. of hot water to the beaker containing the precipitate, stir, allow to settle and decant through the filter as before. Repeat once more. Now transfer the precipitate to the filter by means of a jet of hot water from a wash bottle, using a "policeman" to detach that portion of the precipitate which adheres to the walls of the beaker. Wash the precipitate on the filter with successive portions of hot water until the last washing shows no test for chloride. After the precipitate has been sucked dry at the filter pump for a few minutes, transfer the crucible to an oven and dry at 110°–120° for 12 to 18 hours to constant weight. From the weight of the $BaSO_4$ thus obtained, calculate the percentage of sulfate in the original sample.

220. Exercise No. 15. Determination of Sulfur in Pig Iron, Steel, Washed Metal or Muck Bar. — In these products the percentages of sulfur that may be expected usually lie within the following limits:

Pig Iron	0.12%	or under	
Steel	0.06%.	"	"
Washed Metal	0.03%	"	"
Muck Bar	0.015%	"	"

[3] Instead of such a mixture, a sample of magnesium sulfate, $MgSO_4 \cdot 7 H_2O$, or a standardized solution of this salt, may be used.

As shown by A. Blair,[4] the sulfur present in different kinds of iron and steel, particularly pig iron, may exist in four different forms:

1. That evolved as hydrogen sulfide on treatment with hydrochloric acid; the major portion is in this form.

2. That evolved as an organic sulfide $(CH_3)_2S$, etc., which is very stable and not oxidized by aqua regia, bromine, or ammoniacal hydrogen peroxide; the amount of this is very small and is probably lost by any method in use.

3. That which is not attacked by hydrochloric acid but is oxidized by concentrated nitric acid or aqua regia.

4. That which is unacted on by nitric acid or aqua regia and is only obtainable in solution after fusion with sodium carbonate and potassium nitrate; the amount of this is very small.

There are several methods for obtaining the solution of the sample and at the same time effecting the oxidation of forms (1) and (3) to sulfate, but we will confine our attention to the use of aqua regia.[5]

Procedure.—For percentages of sulfur equal to 0.04% use 5 g. of drillings.[6] Place the drillings in a 400 ml. beaker which is covered by a watch-glass and dissolve by carefully adding a mixture of 40 ml. of 16 M nitric acid and 5 ml. of 12 M hydrochloric acid. After the addition of the acids, place the beaker on a hot-plate until the solution is complete, then add 0.5 g. of sodium carbonate (free from sulfate) and evaporate to dryness but do not bake;[7] add 40 ml. of 12 M hydrochloric acid, evaporate to dryness on a hot-plate and bake at a moderate heat, to dehydrate

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[4] *J. Am. Chem. Soc.*, **19**, 114 (1897).

[5] For the other methods of treatment, the student must be referred to the original sources.   Most of the citations given in this footnote, however, will be found included in the works of Blair, Scott or Treadwell-Hall, see § 11; Noyes & Helmer, *J. Am. Chem. Soc.*, **23**, 675 (1901); Krug, *Stahl u. Eisen*, **25**, 887 (1905); Bamber, *J. Iron Steel Inst.* (London), p. 319 (1894) use conc. nitric acid.

[6] For lower or higher percentages choose a weight of sample that will furnish the same weight of sulfur and use an amount of acid for solution proportionate to the weight of sample taken.

[7] The object of adding the sodium carbonate before evaporation is to furnish sodium ion to fix any free sulfuric acid as sodium sulfate and so prevent any possible loss of sulfur.

silicic acid.   Add 30 ml. of 12 M hydrochloric acid to the residue
and warm until solution has been effected, then evaporate off the
hydrochloric acid until the solution reaches a syrupy consistency;
add 2–4 ml. of 12 M hydrochloric acid and then 30–40 ml. of
hot water.   Filter through a 9 cm. filter paper and wash several
times with 0.1 M hydrochloric acid, keeping the final volume of
filtrate and washings within 100 ml.   To the cold filtrate add
10 ml. of 0.25 M barium chloride, and set aside for at least 24 hours
(see § 217).   Filter the barium sulfate precipitate on a 9 cm.
filter paper and wash it with a hot solution containing 10 ml.
of 12 M hydrochloric acid and 1 g. of barium chloride
($BaCl_2 \cdot 2 \, H_2O$) per liter until washings give no test for iron with
potassium thiocyanate, then wash with hot water until washings
give no test for chlorides with silver nitrate.   Ignite the paper and
precipitate in a weighed platinum crucible, using a Bunsen burner,
add one or two drops of 6 M sulfuric acid to convert any barium
sulfide to sulfate, ignite to drive off the excess sulfuric acid, cool
and weigh.   Repeat the treatment with sulfuric acid, ignite again
and weigh.   Consecutive weighings should agree within 0.1 mg.
A blank determination should be run on all the reagents, and the
results corrected accordingly.

221. Determination of Phosphorus.   General Considerations.
—Phosphorus occurs, for the most part, in salts of H_3PO_4, HPO_3,
$H_4P_2O_7$, H_3PO_3, and in phosphides.   In whatever form it occurs,
its determination depends upon its presence in solution in the
form of orthophosphate.   Meta and pyrophosphates can be
converted to orthophosphate by prolonged boiling in aqueous
solution.   Phosphites and phosphides must be oxidized to ortho-
phosphate.   In the case of the oxidation of phosphide, a very
strong oxidizing agent is required, otherwise some of the phos-
phorus will escape as phosphine PH_3.   Nitric acid alone, or
nitro-hydrochloric acid will not oxidize it; but the addition of
0.1 M potassium permanganate to the boiling nitric acid solution
of the sample will oxidize it (for detail see § 228).   For this reason,
when a sample contains phosphorus in the form of a phosphide,
it must never be dissolved in hydrochloric or sulfuric acids alone.

When all the phosphorus is in solution as orthophosphate, it
can be precipitated either as ammonium phospho-molybdate

$(NH_4)_3PO_4 \cdot 12\ MoO_3 \cdot 2HNO_3 \cdot H_2O$, or as magnesium ammonium phosphate, $Mg(NH_4)PO_4 \cdot 6\ H_2O$. The choice of the particular method depends upon the nature of the accompanying elements.

Table 38 shows those elements which are allowable and those which are not for each of the above precipitations.

Table 38

Non-interfering and Interfering Elements in the Precipitation of Phosphorus

Precipitation of Phosphorus as	Allows Presence of	Requires Absence of
$(NH_4)_3PO_4 \cdot$ $12MoO_3 \cdot$ $2HNO_3 \cdot H_2O$	Members of the alkali and alkaline earth groups, the iron and aluminum group (except tungsten, titanium, and vanadium), the tin and copper groups (except arsenic).	Silicic acid except for very small amounts, titanium, tungsten, vanadium and arsenic.
$Mg(NH_4)PO_4 \cdot$ $6H_2O$	Members of the alkali group, also molybdate ion although a small amount of the latter will be dragged down.	Silicic acid, and all ions that form insoluble phosphates, calcium, barium, strontium, members of the iron and aluminum groups, the copper and tin groups.

Since there are fewer elements interfering with the precipitation of ammonium phospho-molybdate than with the precipitation of magnesium ammonium phosphate, the usual method of procedure is to remove those elements which interfere with the precipitation of ammonium phospho-molybdate and then bring about its precipitation by adding a solution of ammonium molybdate. By filtering and washing this precipitate, we can remove to a considerable extent those elements which would interfere with the subsequent determination of phosphorus.

If the weight of phosphorus being determined is more than about 3 mg., the ammonium phospho-molybdate precipitate is dissolved in NH_4OH and the phosphorus precipitated as $Mg(NH_4)PO_4 \cdot 6\ H_2O$ and weighed as such. The hexahydrate may be ignited and weighed as $Mg_2P_2O_7$.

If the weight of phosphorus being determined is less than about 3 mg., we can dissolve the precipitate in excess standard NaOH solution and determine phosphorus by titrating the excess NaOH with standard HNO_3 solution as explained in §§ 227, 228. An alternative method is to dissolve the precipitate in NH_4OH, acidify with H_2SO_4, reduce the MoO_4^- to Mo^{+++} by passing through a zinc reductor and then to determine phosphorus by titrating with standard $KMnO_4$ solution. This method is explained in detail in § 445.

222. Removal of Elements Interfering with Precipitation of Ammonium Phospho-Molybdate. — The following general procedure will indicate the way and order in which the interfering substances are to be removed, when phosphorus is to be precipitated as ammonium phospho-molybdate. The details in the case of titanium, tungsten, and vanadium, however, are so very much beyond the scope of this work that the student must be referred elsewhere for such information.[8] Silicic acid is first removed by dehydration (see § 216). This operation also will render most of the tungsten insoluble as WO_3, provided concentrated nitric acid has been used for dissolving the sample or during evaporation; titanium as $TiPO_4$ will be found in the dehydrated silica and the recovery of the phosphorus from this must be taken into account; vanadium must be removed by the aluminate method of C. M. Johnson,[9] arsenic is removed by precipitation with hydrogen sulfide. If we assume the removal or absence of the foregoing substances, the phosphorus can be precipitated as ammonium phospho-molybdate in the presence of the remaining substances and the latter got rid of by filtration.

223. Precipitation of Ammonium Phospho-Molybdate. — There are many different directions for the preparation of ammonium-molybdate solution to be used in precipitating ammonium phospho-molybdate. The authors have found the directions given by H. T. Beans and N. E. Johann,[10] to be the most satisfactory in

[8] C. M. Johnson, see reference § 11.

[9] *Ibid.*

[10] N. E. Johann, "A Study of the Composition of Ammonium Phospho-Molybdate and the Determination of Phosphorus," Dissertation, Columbia University, 1921.

giving a dependable solution for this precipitation. They prepare two solutions. Solution 1 is an ammoniacal solution of ammonium molybdate made by dissolving 100 g. of ammonium molybdate (or molybdic oxide) in 400 ml. water and 80 ml. of 15 M NH_4OH. Solution 2 is made by mixing 400 ml. of 16 M HNO_3 with 600 ml. of water. The two solutions are kept separate and mixed only in such portions as are needed for immediate use, the necessary amount of Solution 1 being poured into twice its volume of Solution 2, and the resultant solution being then added to the solution containing the phosphorus. Thus 10 ml. of Solution 1 corresponds to 2 g. $(NH_4)_2MoO_4$ and this amount should be used with 20 ml. of Solution 2 for any amounts of phosphorus up to 20 mg. For larger amounts of phosphorus, correspondingly greater amounts of the two solutions must be used. It is to be noted that ammonium molybdate reagent should always be added in decided excess, namely, about 2 g. $(NH_4)_2MoO_4$ over the amount calculated from the chemical equivalence that 1 g. of $(NH_4)_2MoO_4$ corresponds to about 0.150 g. of P.

In the precipitation of ammonium phospho-molybdate, the closest attention must be given to the following essential details: The solution, before the addition of the molybdate reagent, should have a volume of about 120 ml. and should be acidified slightly with nitric acid, to a pH somewhere between 4.0 and 5.0. It should contain a relatively high concentration of ammonium` nitrate, *i.e.*, 0.5 M (4 g. NH_4NO_3 per 100 ml.). The temperature at the time of precipitation should be about 40° but not greater, as higher temperatures cause the deposition of molybdic oxide MoO_3. The ammonium molybdate reagent should be added rapidly with constant stirring and in the excess previously stated. The solution should be set aside and the precipitate of ammonium phospho-molybdate allowed to digest overnight or longer. When it comes to the filtration and washing of the precipitate, the kind of wash solution to be used depends on what is to be done with the precipitate. If the amount of phosphorus is under 3 mg., it is preferable to use the alkalimetric method of procedure (§ 227) in which event 0.1 M nitric acid is first used to wash the precipitate free of iron and molybdenum salts, and 0.1 M potassium nitrate is next used to wash the precipitate free of the nitric acid.

If the amount of phosphorus is over 3 mg. the phosphorus must be reprecipitated as magnesium ammonium phosphate, in which event the ammonium phospho-molybdate should be washed by decantation (leaving as much of it in the beaker as possible) with a solution which is 0.1 M with respect to nitric acid and 0.1 M with respect to ammonium nitrate until the washings show no brown coloration when tested with hydrogen sulfide. This brown coloration, indicating the presence of molybdenum, is due to MoS_3. It is not possible to wash ammonium phospho-molybdate free of salts with water, even when the water is ice cold, without having some of it run through the filter.

In the precipitation of phosphorus as ammonium phospho-molybdate the above conditions should be observed as closely as possible. Even when considerable care is exercised, it is not possible to obtain precipitates identical in composition. However, they can be made to approximate the formula $(NH_4)_3PO_4 \cdot 12 MoO_3 \cdot 2HNO_3 \cdot H_2O$. Upon being dried at $120°-130°$, this precipitate loses its nitric acid and water and approximates the formula $(NH_4)_3PO_4 \cdot 12MoO_3$. This latter formula contains 1.65% of P, whereas the precipitates actually obtained are likely to vary anywhere between 1.60% and 1.64% [11], or even outside these limits. For this reason, it is not customary to determine phosphorus by weighing this precipitate.

224. Reprecipitation of the Phosphorus as $Mg(NH_4)PO_4 \cdot 6 H_2O$. — Upon the assumption that the washing of the ammonium phospho-molybdate has been done by decantation, part of it will be in the original beaker, the other part on the filter paper through which the supernatant liquid and the washings have been passed. The beaker is placed under the filter paper and 30 ml. of warm 2.5 M ammonium hydroxide is poured over the latter in 10 ml. portions to dissolve any adhering precipitate, after which the filter is washed several times with hot water. The filtrate and washings, whose combined volume should not exceed 100 ml. are caught in the beaker and are used to dissolve the precipitate

[11] Tamm, *Chem. News*, **49**, 208 (1884) found 1.64%; Hundeshagen, *Z. anal. Chem.*, **28**, 141 (1889) found 1.62%; Raben, *ibid.*, **47**, 546 (1908) found 1.64%; Chesneau, *Comptes Rendus*, **146**, 758 (1908) found 1.60%. The factor 1.63% is the one most usually recommended.

which it contains. After the ammonium phospho-molybdate has been dissolved, the solution is made slightly acid to litmus with 3 M hydrochloric acid so that on the subsequent addition of "magnesia mixture," no precipitate will form. It is then cooled to 25°–30°.
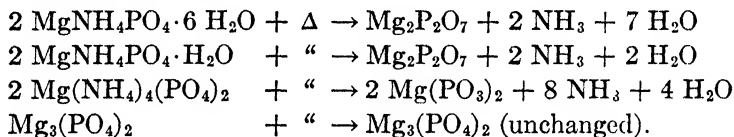
The precipitant used in this determination is "magnesia mixture." It is a solution having the following approximate composition: 0.25 M $MgCl_2$, 1.5 M NH_4Cl, 1.5 M NH_4OH, and is made by dissolving 55 g. of $MgCl_2 \cdot 6 H_2O$ and 70 g. of NH_4Cl in 400 ml. water, adding 90 ml. of 15 M NH_4OH, and diluting to one liter. It should always be filtered before being used. One milliliter of this reagent is approximately the equivalent of 9 mg. of P_2O_5 or 4 mg. of P.

The "magnesia mixture" is slowly added dropwise with constant stirring to the solution containing the phosphorus until a 30–40% excess is present, calculated on the basis of 1 ml. for each 4 mg. of phosphorus present. After the addition of the magnesia mixture, 1.5 M NH_4OH is added slowly with stirring, until the solution is definitely alkaline. The solution is then allowed to stand at room temperature for 1-2 hours.[12] The precipitate of magnesium ammonium phosphate so obtained will always be contaminated somewhat with molybdenum and for precise work it is necessary to resort to reprecipitation as follows: The supernatant liquid is filtered away from the magnesium ammonium phosphate and the latter washed several times with 1.5 M NH_4OH; it is then dissolved in a small amount of 3 M HCl; 2 ml. of magnesia mixture is added and the reprecipitation of the magnesium ammonium phosphate is effected by adding slowly, with stirring, 1.5 M NH_4OH to excess. The solution is allowed to stand at ordinary room temperature (18°–30°) for 1–2 hours until the precipitate of $MgNH_4PO_4 \cdot 6 H_2O$, which is characterized by its crystalline form, has completely settled.

In precipitating phosphorus by means of magnesia mixture, we are confronted with the difficulty of establishing conditions which will invariably yield a precipitate of the definite composition

[12] William A. Worsham, "A Study of the Stability of Magnesium Phosphate ($MgNH_4PO_4 \cdot 6 H_2O$) and a Method of Determining Phosphorus as Magnesium Ammonium Phosphate," Dissertation, Columbia University, 1923.

$MgNH_4PO_4 \cdot 6\,H_2O$. This difficulty arises from the fact that in seeking to establish conditions which will give us a quantitative precipitation of this desired salt we are almost certain to create conditions which will favor the formation of other insoluble phosphates of magnesium, particularly magnesium ammonium phosphate monohydrate $MgNH_4PO_4 \cdot H_2O$, magnesium tetra-ammonium diphosphate $Mg(NH_4)_4(PO_4)_2$, and tri-basic magnesium phosphate $Mg_3(PO_4)_2$. It is at once obvious that if any of these three salts are precipitated along with the hexahydrate, their presence precludes the direct weighing of the precipitate as a measure of the phosphorus present. Recourse has, therefore, been quite generally had to the expedient of igniting the precipitates, because by this treatment the error due to the mixed composition of the precipitate is greatly reduced, though not entirely eliminated, as can be seen by a consideration of the following equations:

$$2\,MgNH_4PO_4 \cdot 6\,H_2O + \Delta \rightarrow Mg_2P_2O_7 + 2\,NH_3 + 7\,H_2O$$
$$2\,MgNH_4PO_4 \cdot H_2O \quad + \text{``} \rightarrow Mg_2P_2O_7 + 2\,NH_3 + 2\,H_2O$$
$$2\,Mg(NH_4)_4(PO_4)_2 \quad + \text{``} \rightarrow 2\,Mg(PO_3)_2 + 8\,NH_3 + 4\,H_2O$$
$$Mg_3(PO_4)_2 \qquad\qquad + \text{``} \rightarrow Mg_3(PO_4)_2 \text{ (unchanged).}$$

If magnesium tetra-ammonium phosphate $Mg(NH_4)_4(PO_4)_2$ is present, the results will be low since in magnesium meta-phosphate $Mg(PO_3)_2$ the ratio of Mg to $(PO_3)_2$ is less than the ratio of 2 Mg to P_2O_7 in the pyrophosphate; on the other hand, if tribasic magnesium phosphate $Mg_3(PO_4)_2$ is present the results will be high.

From the preceding considerations and the further facts that magnesium ammonium phosphate hexahydrate is crystalline, can be easily filtered, and can either be weighed as the hexahydrate or ignited to the pyrophosphate, the desirability of precipitating the magnesium all in the form of $MgNH_4PO_4 \cdot 6\,H_2O$ is apparent. We will now proceed to discuss the necessary conditions for this. In any solution of a phosphate we have the following equilibrium existing between the several ions and the undissociated acid,

$$H_3PO_4 \rightleftarrows H_2PO_4^- \rightleftarrows HPO_4^= \rightleftarrows PO_4^\equiv ,$$

$$\xleftarrow{\hspace{2cm}} \qquad\qquad \xrightarrow{\hspace{2cm}}$$
$$\text{acid} \qquad\qquad\qquad\qquad \text{alkaline}$$
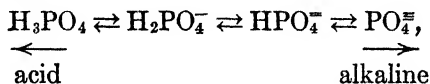
the relative distribution of the several components depending upon the concentration of hydrogen ion of the solution. If the solution is made acid the concentration of those components at the left will be built up at the expense of those at the right, and, conversely, if the solution is made alkaline the concentration of those components at the right will be built up at the expense of those at the left. If a solution containing magnesium ion is added to a solution of a phosphate, we have the possibility of precipitating several phosphates according to which solubility products are exceeded:

$$[Mg^{++}] \times [H_2PO_4^-]^2 > K_{Mg(H_2PO_4)_2}, \tag{1}$$

$$[Mg^{++}] \times [HPO_4^=] > K_{MgHPO_4}, \tag{2}$$

$$[Mg^{++}]^3 \times [PO_4^{\equiv}]^2 > K_{Mg_3(PO_4)_2}. \tag{3}$$
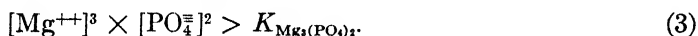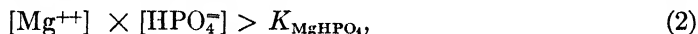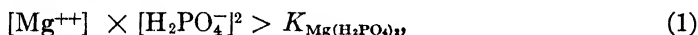
Moreover, if the solution from which precipitation is being effected is very alkaline, we have the further possibility of precipitating magnesium hydroxide by exceeding its solubility product,

$$[Mg^{++}] + [OH^-]^2 > K_{Mg(OH)_2}. \tag{4}$$
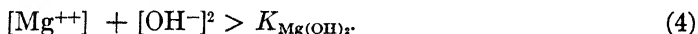
By making the solution sufficiently acid we can prevent the precipitation of any of the four precipitates. If now to such a solution we add dropwise and with constant stirring a dilute solution of ammonium hydroxide, we will build up the concentration of $HPO_4^=$ and $PO_4^{\equiv}$ ions and cut down the concentration of the $H_2PO_4^-$ ion (see § 126). Consequently, the greatest danger of precipitating $Mg(H_2PO_4)_2$ is at the start when we begin adding the ammonium hydroxide, because this is the time when the concentration of $H_2PO_4^-$ ion will be at its maximum. Now it so happens for the concentrations of Mg^{++} employed in analytical work and the relative distribution that exists between $H_2PO_4^-$ and $HPO_4^=$ that the solubility product of $Mg(H_2PO_4)_2$ will not have been reached at the juncture when the solubility product of $MgHPO_4$ will have been exceeded; consequently, we can obtain $MgHPO_4$ without a simultaneous precipitation of $Mg(H_2PO_4)_2$. As we continue to make our solution more alkaline, however, we are confronted by the possibility that the concentration of $PO_4^{\equiv}$ may be built up to a point where the solubility product of $Mg_3(PO_4)_2$ will be exceeded, an occurrence which would result

either in the precipitation of some $Mg_3(PO_4)_2$ or in the transposition to this salt of more or less of the $MgHPO_4$ previously formed; or we might even continue making the solution so alkaline that $Mg(OH)_2$ would be precipitated. To obviate these undesirable occurrences, recourse must be had to some method by which the concentration of hydroxyl ion in the solution shall not exceed an undesirable value. The method which is used for this purpose is to employ dilute ammonium hydroxide solution in slight excess and to buffer the ammonium hydroxide by having present ammonium chloride. Under these conditions the concentration of $PO_4^{\equiv}$ will not be built up to the point where $Mg_3(PO_4)_2$ will be precipitated, nor will the concentration of OH^- ion be sufficient to cause the precipitation of $Mg(OH)_2$; on the other hand, the concentration of $HPO_4^{=}$ will be great enough to insure the quantitative precipitation of $MgHPO_4 \cdot 6\,H_2O$ which, in the presence of the excess of ammonium hydroxide, becomes ammoniated [13] and passes over into magnesium ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$.

Ammonium chloride materially increases the solubility of magnesium ammonium phosphate even in the presence of considerable concentrations of ammonium hydroxide, but exact figures on this score seem to be lacking. While the presence of ammonium chloride is necessary during the precipitation of magnesium ammonium phosphate to prevent the precipitation of magnesium hydroxide, its concentration should not much exceed 0.4 M.

It is important that the precipitation of $MgNH_4PO_4 \cdot 6\,H_2O$ take place at about ordinary room temperature (18°–30°) in order to insure the absence of $MgNH_4PO_4 \cdot H_2O$. The latter salt forms and is stable in solution at temperatures above 62°; if once formed, it takes about twenty-four hours or so at room temperature to be transposed to the hexahydrate.

225. Filtration, Washing and Drying of $MgNH_4PO_4 \cdot 6\,H_2O$. — If phosphorus is to be weighed as $Mg_2P_2O_7$, the $MgNH_4PO_4 \cdot 6\,H_2O$ precipitate may be collected on a Gooch crucible or filter paper. A porous bottom crucible is less desirable as it may crack at the temperature required for ignition. After filtration, it is washed free of salts with 1.5 M NH_4OH.

[13] Gibbs, *Amer. J. Sci.*, **3**, 114 (1873).

If the phosphorus is to be weighed as $MgNH_4PO_4 \cdot 6H_2O$, it may be collected on a Gooch crucible or a porous bottom crucible. It is washed free of chlorides with 1.5 M NH_4OH, after which it is washed two or three times with 15 ml. portions of 95% alcohol and finally twice with 15 ml. portions of ether.[14] After this, it is sucked dry at the filter pump for 10 minutes. The crucible is then allowed to stand in the air or in the desiccator for 15–20 minutes. It is then weighed at once as $MgNH_4PO_4 \cdot 6\,H_2O$.

Magnesium-ammonium phosphate hexahydrate $MgNH_4PO_4 \cdot 6H_2O$ is one of the most soluble precipitates with which we have to deal in quantitative analysis, its solubility in pure water being about 65 mg. per liter at 10°. In the presence of excess of ammonium hydroxide, this solubility is very materially cut down, owing to the mass action effect of the ammonia in repressing the hydrolysis of the salt,

$$MgNH_4PO_4 + H_2O \rightleftarrows MgHPO_4 + NH_4OH.$$
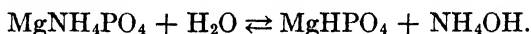
According to Stünkel, Wetzke, and Wagner [15] the following amounts of $MgNH_4PO_4 \cdot 6\,H_2O$ are soluble per liter of ammonium hydroxide of the concentration given:

Concentration NH_4OH	0.12M	0.3M	0.6M	1.2M	1.7M
mg. $MgNH_4PO_4 \cdot 6H_2O$	12	6	3	1	0.8

For this reason, it is the practice in washing magnesium ammonium phosphate to use 1.5 M NH_4OH as the wash solution.

As regards its stability, the hexahydrate does not suffer any change in weight at room temperatures (18°–30°) and under ordinary laboratory atmospheric conditions; if placed in a desiccator over anhydrous calcium chloride, it will lose weight at the rate of about 1 mg. in 24 hours for each gram of sample, the temperature being 18°–30°. At 50° in a drying oven the loss in weight is very much greater, amounting to about 28 mg. in 24 hours for each gram of sample. By drying the precipitate by means of alcohol and ether, more nearly correct results are obtained than by the application of heat.[16]

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[14] A good grade of ether with the usual 3% alcohol in it is perfectly satisfactory.

[15] C. Stünkel, T. Wetzke, and F. Wagner, *Z. anal. Chem.*, **21**, 353 (1882).

[16] For reference, see footnote 12, § 224.

When phosphorus is determined by precipitating first as ammonium phospho-molybdate, followed by precipitation as magnesium ammonium phosphate hexahydrate, the precision obtained depends almost entirely on the second part of the method, because phosphorus, generally speaking,[17] is quantitatively precipitated as ammonium phospho-molybdate. Assuming due care in the precipitation of $MgNH_4PO_4 \cdot 6H_2O$, and in reprecipitating it to free it of molybdate dragged down the first time, and assuming due care in washing, drying, and weighing the $MgNH_4PO_4 \cdot 6 H_2O$, we can probably claim a precision of 5 to 20 parts per 1,000 for amounts of phosphorus ranging between 3 and 50 mg.

226. Ignition of $MgNH_4PO_4 \cdot 6 H_2O$ to $Mg_2P_2O_7$. — If it is desired to effect the conversion of the hexahydrate to the pyrophosphate, according to the reaction,

$$2 \ MgNH_4PO_4 \cdot 6 \ H_2O + \Delta \rightarrow Mg_2P_2O_7 + 2 \ NH_3 + 7 \ H_2O,$$
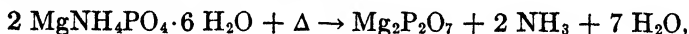
a temperature of 750° and prolonged heating of an hour or so are necessary. In practice it is customary to employ higher temperatures (1100°–1300°) and a shorter time for this conversion, making use of a Meker burner or a blast lamp for 30 minutes. The heating is always repeated until constant weight is obtained. The phosphorus is weighed as $Mg_2P_2O_7$. If magnesium ammonium phosphate has been collected on a filter paper, then, in the subsequent ignition of the filter paper, some of the resulting carbon seems to become enclosed by the precipitate and it is often a very difficult matter to burn off this carbon. This carbon gives rise to so-called "black precipitate"[18] which, once it has been formed, baffles all attempts to make it white again, either by prolonged ignition or treatment with oxidizing agents like nitric acid or ammonium nitrate. Undoubtedly, there is some error introduced by accepting the results based upon "black precipitates" of magnesium pyrophosphate, but it is generally

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[17] In the case of steels where the amount of phosphorus is very small and the amount of iron very large, it appears that phosphorus is not always quantitatively precipitated as ammonium phospho-molybdate, probably due to the fact that some of it is tied up as the complex or undissociated ferric phosphate.

[18] For a discussion of interesting phenomena connected with the ignition of magnesium ammonium phosphate see S. J. Kiehl and H. B. Hardt, *J. Am. Chem. Soc.*, **55**, 605 (1933); *ibid.*, **55**, 3555 (1933).

believed that the error is not large and it has been more or less the custom to accept such results.

It is imperative with respect to the ignition of magnesium pyrophosphate that consecutive weighings, each preceded by at least thirty minutes of strong ignition, should agree within 0.2 mg. If the ignited precipitate continually loses weight, it indicates the presence of magnesium meta-phosphate $Mg(PO_3)_2$ which is losing P_2O_5 by volatilization,

$$2\ Mg(PO_3)_2 + \Delta \rightarrow Mg_2P_2O_7 + P_2O_5$$
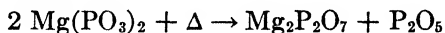
in which event the results are valueless.

If platinum crucibles are employed in this ignition, great care must be exercised to insure that they are kept entirely out of the reducing zone of the flame, as otherwise some of the pyrophosphate will be reduced to phosphorus with the consequent ruining of the crucible.

227. Alkalimetric Titration of Phosphorus. — The alkalimetric titration method of determining phosphorus is particularly suitable when the weight of phosphorus present is less than 3 mg. In this method, the phosphorus is precipitated as ammonium phosphomolybdate. After washing free of salts with 0.1 M nitric acid, it is washed with 0.1 M potassium nitrate until the washings are free of acid as indicated by methyl orange. The precipitate is then treated with excess standard sodium hydroxide. We can consider the reaction taking place to be:

$$2\ (NH_4)_3PO_4 \cdot 12\ MoO_3 + 46\ NaOH \rightarrow 2(NH_4)_2HPO_4 +$$
$$23\ Na_2MoO_4 + (NH_4)_2MoO_4 + 22\ H_2O.$$
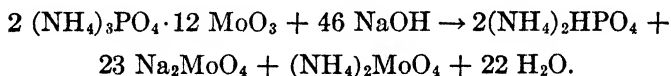
The excess sodium hydroxide is determined by back titration with standard nitric acid using phenolphthalein as indicator. From the volume and concentration of the sodium hydroxide solution used on the precipitate, the weight of phosphorus can be calculated from the relationship,

$$23\ NaOH \equiv P.$$

Since the precipitate may contain a larger or a smaller proportion of MoO_3 than is indicated by the formula $(NH_4)_3\ PO_4 \cdot 12$

MoO_3, it is advisable to run a control determination of a sample containing a known weight of phosphorus, maintaining, as closely as possible, the conditions used in the unknown determination.

Precision.— The precision which is obtainable by this method for amounts of phosphorus up to 3 mg. is probably not better than 5 parts per 1,000 because of the small quantities of phosphorus involved and because of the further fact that the presence of phosphate ion [19] in the solution causes the end point of the titration to be somewhat uncertain.

The details of this method are given in the following paragraph where it is applied to the determination of phosphorus in plain carbon steels or iron.

228. Exercise No. 16.   Determination of Phosphorus in Plain Carbon Steels or Iron.[20]   Alkalimetric Method. — The content of phosphorus to be expected in this class of products is a maximum of 0.05% for good grades of steels and 0.5–0.9% for pig and cast irons.   The phosphorus in iron or steel exists as a phosphide so that the first step in analysis is the oxidation of the phosphorus to ortho-phosphate ion.   This oxidation is best accomplished by dissolving the sample in 6 M nitric acid, and as soon as solution is effected, by adding 10 ml. or so of 0.1 M potassium permanganate and boiling to effect the oxidation of the phosphorus.

Procedure.—Weigh out 2 g. of steel drillings or 1–2 g. of pig iron, place in a 400 ml. beaker and add 50 ml. of 6 M nitric acid, keeping the beaker covered with a watch-glass and warming gently until solution is completed (with pig irons some undissolved graphite will be left at this juncture and it is preferable to let it stay for the time being).   Add 10 ml. of 0.1 M potassium permanganate and boil until the pink color disappears; the excess of permanganate is reduced by this procedure and the manganese precipitates out as hydrated manganese dioxide; this precipitate is dissolved by adding sodium sulfite solution or ferrous sulfate solution in small portions until the solution clears

[19] Johann, see footnote, § 223.

[20] Special alloy steels containing titanium, tungsten, or vanadium require special treatment because of the presence of these interfering substances, see § 221.

up. At this point with pig iron any undissolved graphite should be filtered off so as to have a clear solution for the precipitation of the ammonium phospho-molybdate. Cool the solution to about 50° and neutralize with 6 M ammonium hydroxide until the solution is deep red in color (usually about 40 ml. will be required); then add 3 M nitric acid until the red color changes to orange. Adjusting the temperature of the solution to approximately 40°, add 30 ml. of molybdate reagent (10 ml. of Solution 1 poured into 20 ml. of Solution 2, § 223) and set aside to digest overnight, or longer if no precipitate has appeared by morning.[21] Filter on a 9 cm. filter paper and wash with 0.1 M nitric acid until free of iron (thiocyanate test) and then with 0.1 M potassium nitrate until free of acid (methyl orange test). Place the filter paper and its precipitate in a glass-stoppered Erlenmeyer flask and add 20 ml. of 0.1 M standard sodium hydroxide solution, shake violently to disintegrate the filter paper and hasten the solution of the ammonium phospho-molybdate. If after agitation any of the precipitate remains undissolved, add 10 ml. more of the standard sodium hydroxide solution and shake again. When the precipitate is dissolved add 50 ml. of water and 3 drops of phenolphthalein solution and titrate back the excess of sodium hydroxide with 0.1 M standard nitric acid. From the amount of sodium hydroxide used up by the precipitate, calculate the amount of phosphorus present.[22]

An alternative method of determining phosphorus is given in § 445.

229. Exercise No. 17. Determination of Phosphoric Anhydride in Apatite. — Apatite is a phosphate rock of the essential composition $(CaF)Ca_4(PO_4)_3$ in which some of the calcium is usually replaced by small amounts of magnesium, iron, or aluminum, some of the fluorine by chlorine, and some of the phosphate by small amounts of silicate. Its theoretical compo-

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[21] Some authors recommend shaking the solution violently for four to five minutes after the addition of the molybdate reagent and then filtering within 30 minutes, but it seems that about 5% of the phosphorus remains in solution by this procedure.

[22] From the reaction given 1P ≡ 23 NaOH; hence verify that 1 ml. 0.1 M NaOH ≡ 0.0001349 g. P.

sition as well as the composition of an actual specimen is given herewith:

	Theoretical [23]	Actual [24]
P_2O_5	42.25%	40.37%
CaO	55.56	53.05
F	3.76	3.31
Cl	....	.44
Al_2O_3	....	.61
Fe_2O_3	....	.15
MgO	....	.15
Insoluble matter	....	3.89
CO_2	....	.03
	101.57%	102.00%

As already mentioned in § 221 *et seq.*, any silicic acid that is present must first be removed and then the phosphate precipitated as ammonium phospho-molybdate, in order to separate it from the elements which form insoluble phosphates, *i.e.*, calcium, magnesium, iron, aluminum, etc.

Procedure. — Assuming that the sample has been properly prepared with respect to its homogeneity (§ 13) and ground to a fineness of 50–70 mesh, weigh out into a beaker or casserole 0.180–0.200 g., add 15 ml. of 6 M nitric acid, cover the vessel with a watch-glass and warm gently until solution has been effected; then evaporate to dryness on the water bath (see § 216) and maintain at 100°–115° for about an hour to dehydrate the silicic acid. Add 25 ml. of 6 M nitric acid and heat for several minutes to dissolve the soluble portion, filter off the silica on a 7 cm. filter paper and wash with as little warm water as possible. After six washings test the next washing for the presence of calcium by collecting 2–3 ml. of it in a test tube and making alkaline with ammonia, — a turbidity indicates presence of calcium owing to the formation of calcium phosphate. If calcium is found present join the contents of the test tube with the main filtrate and con-

[23] Dana, see reference, § 1.

[24] Hoffman, *Report Geological Survey*, Canada, 1 H (1879).

tinue washing until washings are free of calcium, joining all tests with the main filtrate. The final volume of filtrate and washings must not exceed 100 ml. After washing, the next step is to neutralize most of the excess of nitric acid in the filtrate by cautiously adding 6 M ammonium hydroxide until the precipitate of calcium phosphate first produced fails to redissolve, and then by adding a few drops of nitric acid until the solution clears up.

Warm the acidulated solution to 40° and add 90 ml. of molybdate reagent (30 ml. of Solution 1 poured into 60 ml. of Solution 2, § 223); set aside for at least 4 hours or more, preferably overnight. After digestion, filter off the supernatant liquid through a 7 cm. filter and test it with molybdate reagent to see if precipitation has been complete.[25] Granting that complete precipitation has taken place, retain as much of the ammonium phospho-molybdate as possible in its original beaker and wash by decantation (using as a wash solution one which is 0.1 M with respect to nitric acid and 0.1 M with respect to ammonium nitrate) until the washings give no turbidity when tested for calcium with ammonia and ammonium oxalate. When washing is complete place the beaker containing the main bulk of the precipitate under the filter paper through which filtration has been effected, and pour over the filter paper several 10 ml. portions of 2.5 M ammonium hydroxide to dissolve any precipitate tha\ might have been collected; then wash the filter paper carefully with five 10 ml. portions of hot water. The final volume of filtrate and washings must not exceed 100 ml. By this treatment the precipitate on the filter paper as well as the main portion in the beaker should be dissolved; if, however, the latter remains undissolved, add more ammonia cautiously until solution is effected.

To the clear ammoniacal solution add 3 M hydrochloric acid cautiously until the solution is slightly acid to litmus paper, then add dropwise an amount of magnesia mixture calculated to be 40% in excess over that demanded by the phosphorus present (see § 224); next add cautiously and with constant stirring 1.5 M ammonium hydroxide until the solution is definitely alkaline. Then allow the solution to stand at room temperature for 1–2

[25] If precipitation has not been complete rejoin the filtrate with the precipitate, add more molybdate reagent and set aside for further precipitation.

hours.   As pointed out in § 224, the precipitate of magnesium ammonium phosphate so obtained will always be contaminated somewhat with molybdenum so that for precise work it is necessary to resort to reprecipitation in order to obtain a pure precipitate of $MgNH_4PO_4 \cdot 6 H_2O$.   The details of this part of the procedure will be found in § 224, and should be followed accordingly.   The precipitate may be ignited to $Mg_2P_2O_7$.   From the weight of $MgNH_4PO_4 \cdot 6 H_2O$ or $Mg_2P_2O_7$ found calculate the percentage of P_2O_5 in the sample.

230. Exercise No. 18.   Determination of Silica, Sulfur and Phosphorus in an Iron Ore. — The constituents that are most frequently called for in the analysis of an iron ore are iron, silica, sulfur and phosphorus.[26]   The iron is most easily determined in a small separate portion, while a much larger portion is taken for the silica, sulfur and phosphorus.   The ores of iron which are usually encountered are:

Red Hematite	Fe_2O_3
Limonite	$2 Fe_2O_3 \cdot 3 H_2O$
Magnetite	Fe_3O_4
Siderite	$FeCO_3$

Procedure. — It is presupposed that the sample furnished for analysis has been carefully taken in accordance with the principles of sampling, and that it has been ground to a fineness of 100 mesh, as both these steps are essential preliminaries to the analysis.   A determination of moisture in the samples should be made and included in the report, and the temperature at which the moisture is driven off should also be stated (105°–110°).   The percentages of the several constituents should be calculated to the dry basis and so reported.

Weigh accurately about 5 g. of the ore and transfer to a porcelain casserole.   Cover the casserole with a watch-glass and add about 10 ml. of 16 M HNO_3 and 50 ml. of 12 M HCl.   Digest on the

[26] Occasionally, in addition to these, some or all of the following are required: aluminum, titanium, manganese, calcium and magnesium.   For methods dealing with the determination of these elements in iron ores, see U. S. Steel Corporation, "Methods for the Commercial Sampling and Analysis of Iron Ores," see reference § 11; also Fay, p. 15, see reference § 11.

hot-plate for about 15 minues. Dilute with about 100 ml. of water and digest again for about 15 minutes. Filter while hot, collecting the filtrate in another casserole. Wash a few times with hot water and transfer the residue to the filter. Place the casserole containing the filtrate on the hot-plate and concentrate by evaporation. Place the filter in a platinum crucible and burn the paper at low temperature. Care must be taken to avoid loss of sulfur. Add anhydrous sodium carbonate (five or six times the weight of the residue) and about 0.2 g. of sodium nitrate, mix with a dry glass rod and fuse for about a half hour with the usual precautions. While the crucible is cooling, spread the contents over the sides and bottom as previously described and, when cold, place in a small beaker, cover with a watch-glass and add hot water. After digesting for a short time, add in small portions about 20 ml. of 12 M HCl and digest until the fused mass is detached from the crucible. Remove the crucible, washing the solution and silica from it into the beaker. When the fused mass is decomposed, transfer the solution and silica from the beaker to the casserole containing the main solution and continue the evaporation to dryness. The temperature at which this evaporation takes place must not exceed 120°. Remove the casserole from the hot-plate and moisten the residue with 10 ml. of 12 M HCl and then add about 50 ml. of boiling water. Digest on the hot-plate for a few minutes and then decant the solution through a small filter. Again treat the residue with acid and water and repeat as long as the residue contains iron, as shown by its color. Finally transfer the residue to the filter, removing the residue from the casserole with a rubber-capped rod in the usual way. Wash thoroughly with hot water. From 1 to 3% of the total silica present will pass into this filtrate and, hence, at this point it must be estimated whether a second evaporation of the filtrate is necessary. If the amount of silica present warrants this second evaporation, it is carried out exactly as the first and the. filters containing the silica are then placed in an unweighed platinum crucible and the ignition to constant weights is carried out as usual, using a blast or Meker burner to complete the ignition. Moisten the residue with water and add 2 drops of 9 M H_2SO_4 and then about 5 ml. of concentrated HF solution. Evaporate to

dryness under the hood. Ignite, first with the Bunsen and finally with blast or Meker burner and weigh. If more than a very slight residue remains, repeat the treatment with H_2SO_4 and HF and ignition to constant weight. From the loss in weight calculate the percentage of silica in the ore.

The residue in the platinum crucible after the removal of the silica may contain, among other compounds, barium sulfate and titanium phosphate. Add about 1 g. of anhydrous sodium carbonate and fuse. Leach the fused mass with hot water and filter through a small paper. Wash with hot water. Reject the residue. Add the filtrate to the main solution containing the sulfate and phosphate. Pour this main solution, cooled to room temperature, into an excess of ammonium hydroxide solution (20 ml. 15 M NH_4OH diluted with water to 400 ml.). Heat to boiling, filter and wash with hot water until the filtrate shows only a slight test for chloride. Concentrate the filtrate to a volume of 150–200 ml., make very slightly acid with hydrochloric acid and determine the sulfate as barium sulfate exactly as described in § 219. From the result thus obtained, calculate the percentage of sulfur in the ore.

The precipitate of ferric hydroxide, etc., contains all the phosphorus of the ore as ferric phosphate. Transfer as much of this precipitate as possible to a 250 ml. beaker by means of a small porcelain spoon or spatula. Place a clean beaker under the funnel and dissolve the precipitate remaining on the filter in hot 3 M HNO_3. If the precipitate does not dissolve in a moderate amount of the acid, replace the beaker under the funnel by a clean beaker, heat the solution which has run through the filter and return it through the filter again and again till all the precipitate has dissolved from the filter. Wash the filter with water until most of the iron has been removed. Pour this acid solution into the beaker containing the major part of the ferric hydroxide precipitate. Wash out the beaker and add the washings to the main solution and then heat until the precipitate is completely dissolved. If necessary add more acid, but a large excess should be avoided. The volume of this solution should not exceed 150 ml. If greater than this, concentrate by evaporation. Carefully neutralize this solution with ammonium hydrox-

ide until a faint but permanent precipitate forms, then add about 5–10 ml. 16 M nitric acid until the deep red color of the solution changes to an orange yellow; after this change add 10 g. of ammonium nitrate. Heat the solution to about 40° and add 90 ml. of molybdate reagent (30 ml. of Solution 1 poured into 60 ml. of Solution 2, § 223); then set aside for 14–24 hours. Filter the "yellow precipitate" through a 9 cm. filter and wash with a solution consisting of 0.5 M ammonium nitrate and 0.5 M nitric acid. (This solution is most easily prepared by mixing 3 M nitric acid and 3 M ammonium hydroxide in the proportion of two moles of the former to one of the latter and diluting down to the desired molar concentration.) Wash the precipitate and filter until the successive portions of the washings show only a slight brown color when treated with hydrogen sulfide. Notice that it is not necessary to transfer the precipitate from the filter to the beaker but merely to wash it thoroughly. When this has been done, place the beaker in which the precipitation was made under the funnel and pour hot 3 M ammonium hydroxide through the filter until the precipitate has dissolved. Wash the filter with water until the total volume of the solution is about 100 ml. Now add 12 M hydrochloric acid to the solution until the latter is faintly acid and cool to room temperature (18°–25°). To this slightly acid solution add dropwise an amount of magnesia mixture calculated to be 40% in excess over that demanded by the phosphorus present (see § 224). Next add cautiously, and with constant stirring, 1.5 M ammonium hydroxide until the solution is definitely alkaline. Allow the solution to stand at room temperature for 1–2 hours. Filter the precipitate through a weighed Gooch crucible and wash with 1.5 M. ammonium hydroxide until free of chlorides,[27] then with three or four 15 ml. portions of 95% alcohol, and then with two 15 ml. portions of ether; suck dry at the filter pump for 10 minutes, place in the desiccator for 20 minutes and weigh as $MgNH_4PO_4 \cdot 6\,H_2O$. From the weight of the hexahydrate calculate the percentage of phosphorus in the ore.

231. Use of Factor Values in Gravimetric Determinations. — By an application of the principle developed in § 160 it is possible

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[27] If desired, the precipitate, after being washed free of chlorides, can be ignited to $Mg_2P_2O_7$.

to choose such a weight of sample for analysis that each milligram of precipitate shall correspond to a definite percentage of con-stituent in the sample. Where a series of determinations of the same constituent is being made, this device saves a great deal of time since it obviates the necessity of making an individual calculation for each determination. The general method of arriving at the desired weight is shown herewith:

Let

W = desired weight of sample in grams,

p = % constituent to be represented by 1 mg. of precipitate,

w = weight in milligrams of precipitate from W,

f = number of grams of constituent corresponding to 1 g. of precipitate.

Then

$$\frac{fw}{1000} = \text{grams of constituent in } W. \tag{1}$$

Also by the condition that has been set, we have

$$wp = \% \text{ constituent in sample.} \tag{2}$$

Whence

$$\frac{W \cdot wp}{100} = \text{grams of constituent in } W. \tag{3}$$

Equating (1) and (3), we get

$$\frac{W \cdot wp}{100} = \frac{fw}{1000}; \text{ or } W = \frac{f}{10\,p}. \tag{4}$$

From this we see that if W is taken equal to f, p is equal to 0.1, that is, each milligram of precipitate will correspond to 0.1% constituent in the sample. If W is taken equal to one-tenth of f, p is equal to 1, that is, each milligram of precipitate will correspond to 1% constituent in the sample.

Example. — Suppose that it is required to weigh out such a quantity of pig iron for analysis that each milligram of barium sulfate precipitate will correspond to 0.0025% sulfur in the sample. We have

$$W = \frac{0.1374}{10 \times 0.0025} = 5.496 \text{ g.}$$

It is easy to verify the foregoing. Thus let us assume that the weight of $BaSO_4$ obtained from 5.492 g. sample was 0.050 g. This multiplied by 0.0025 gives 0.125% as the percentage of S in the sample. If we compute the percentage by using the factor for S in $BaSO_4$ we have $\dfrac{0.050 \times 0.1374}{5.496} = 0.00125$ g. S in 1 g. which is equal to 0.125%.

232. Examples.

1. What error, expressed in percentage of sulfur, would result if, in the analysis of an ore containing 8.34% of sulfur, 10% of the $BaSO_4$ were reduced to BaS by the filter paper and so weighed?

Ans. Error = 0.23%.

2. 5.018 g. of a sample of crucible iron yielded 0.0159 g. barium sulfate. What was the content of sulfur? Ans. 0.044%.

3. 4.160 g. of the same sample of crucible iron as mentioned in Example 2 gave 0.0640 g. magnesium pyrophosphate. What was the content of phosphorus? Ans. 0.43%.

4. 10.00 g. of potash marl (soil) was dissolved and made up to 500 ml. (For the methods of the Association of Official Agricultural Chemists, see Doolittle, reference given in § 11.) 50 ml. of this solution was used for the determination of the phosphorus by the alkalimetric method (§ 188). The "yellow precipitate" was dissolved in 20.00 ml. of 0.1086 M NaOH; the excess of NaOH was titrated back with 0.1509 M HNO_3 in the presence of phenolphthalein solution as indicator, the back titration requiring 9.84 ml. of the acid. What was the content of phosphorus calculated as P_2O_5? Ans. 0.22%.

5. How many grams of steel should be taken for analysis in order that each milligram of barium sulfate shall correspond to 0.004% sulfur?

Ans. 3.433 g.

6. How many grams of steel should be taken for analysis in order that each milligram of ammonium phospho-molybdate found shall correspond to 0.001% phosphorus? Ans. 1.654 g.

7. How many grams of iron ore must be taken in order that each milligram of magnesium pyrophosphate shall correspond to 0.004% P in the ore? Ans. 6.97 g.

8. A sample of crucible iron, melted in an oil-fired furnace, was analyzed for its silicon content; weight of sample, 4.165 g.; weight of platinum

crucible, 19.2195 g.; weight of crucible + crude SiO_2, 19.4688 g.; weight of crucible and residue after treatment with H_2SO_4 + HF, 19.2276 g. What was the percentage of silicon? What was the weight of residue (probably Fe_2O_3) in the crucible after the HF treatment?

Ans. 2.72%. 0.0081 g.

9. A sample of electric furnace iron was analyzed for its silicon content; weight of sample 4.165 g., weight of SiO_2 by loss after treatment with H_2SO_4 + HF, 0.1269 g. What was the percentage of silicon?

Ans. 1.29%.

10. In a determination of sulfur the $SO_4^=$ was quantitatively precipitated when $BaCl_2$ solution was added. The precipitate of $BaSO_4$ contained co-precipitated K_2SO_4. Will the results be low or high? Explain.

11. In a determination of sulfur, $SO_4^=$ was quantitatively precipitated when $BaCl_2$ solution was added. The precipitate of $BaSO_4$ formed contained co-precipitated $Ba(NO_3)_2$. Will the results be low or high? Explain.

12. The sulfur in a 0.1421 g. sample of pyrite ore is oxidized to sulfate and precipitated as $BaSO_4$. The precipitate obtained weighed 0.4701 g. Assuming that all the sulfur in the original ore was present as pyrite, FeS_2, calculate the per cent of pyrite in the ore.

13. Assume that in Example 12 all the iron in the ore is present as FeS_2. Calculate the per cent of iron in the ore.

14. In the analysis of a 0.1753 g. sample of apatite 0.1114 g. $Mg_2P_2O_7$ was obtained. Calculate the per cent of P_2O_5 in the sample.

CHAPTER XII

DETERMINATION OF CALCIUM AND MAGNESIUM AND THE ANALYSIS OF CARBONATE ROCKS

233. Determination of Calcium. — There are several methods for the determination of calcium but they are nearly all based upon the procedure of getting calcium into solution as calcium ion and then precipitating the latter as calcium oxalate by means of a solution of ammonium oxalate, according to the reaction

$$Ca^{++} C_2O_4^- \rightarrow CaC_2O_4.$$

The calcium oxalate may be ignited to calcium oxide and the latter compound weighed, or the oxide may be converted by means of sulfuric acid into calcium sulfate and weighed in this form. Another alternative is to dissolve the calcium oxalate in dilute sulfuric acid and to titrate the oxalate ion by means of standard permanganate solution. The principle upon which this oxidimetric method is based is described in § 333.

234. Precipitation of Calcium Oxalate. — In the precipitation of calcium, oxalate ion is selected as the precipitant in preference to other ions, such as fluoride or carbonate ion, because the calcium oxalate formed is the most insoluble salt of calcium and because its crystalline character permits of easy and thorough washing. The carbonate is much more soluble than the oxalate, and the fluoride, which possesses about the same solubility as the carbonate, has the additional objectionable feature of precipitating in a slimy condition.

In the precipitation of calcium oxalate, care must be taken that the solution is free of all forms of silicic acid, likewise all ions that give insoluble oxalates, namely, ions of the copper, iron and aluminum groups and also strontium ion. The following ions are permissible: magnesium, barium, sodium, potassium, and ammonium. It is to be remarked, however, that the first four of these are always more or less co-precipitated with calcium oxalate and that double

precipitation with intervening filtration is always necessary when they are present. The presence of magnesium ion deserves special attention and will be considered in § 235.

The solution from which calcium is to be precipitated should have a volume of about 200 ml. and may contain as much as 300 mg. of calcium ($\equiv$ 420 mg. CaO). This solution should contain enough hydrochloric acid to make its pH about 4. Precipitation should be effected from the boiling solution by adding dropwise a 0.25 M solution of ammonium oxalate until an amount has been added which is equivalent to the combined amounts of calcium and magnesium present plus 10% of this amount, and then by adding dropwise a 3 M solution of ammonium hydroxide until the solution is alkaline.

235. Interference of Magnesium Ion in Precipitating Calcium Oxalate. — Calcium and magnesium often have to be determined from the same solution after the removal of the iron and aluminum group by means of ammonium hydroxide and ammonium chloride. This is particularly true in the analysis of limestones, cements, rocks, etc.

The precipitation of calcium oxalate in the presence of magnesium ion always results in the co-precipitation of magnesium oxalate. This necessarily requires re-solution of the precipitate and reprecipitation under conditions which reduce the tendency of magnesium oxalate to separate out with the calcium. The co-precipitation of magnesium, which amounts to about 0.1%–0.2% of the amount of magnesium present when there is no excessive disparity in the relative proportions of magnesium and calcium, is reduced to a minimum by a second precipitation by causing the precipitation to take place from as acid a solution as possible. The solution must be acidulated with enough hydrochloric acid to repress the concentration of oxalate ion to a point where the solubility product of calcium oxalate is not reached. Oxalic acid is a comparatively weak acid and, hence, any increase in the hydrogen ion concentration will result in a corresponding decrease in oxalate ion concentration, according to the scheme,

$$H_2C_2O_4 \rightleftarrows HC_2O_4^- \rightleftarrows C_2O_4^-$$

$$\xleftarrow{\text{acid}} \qquad \xrightarrow{\text{alkaline}}$$
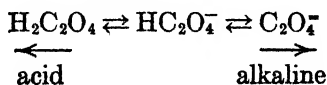
On slow addition of dilute ammonium hydroxide, the hydrogen ion concentration is gradually decreased, due to its removal to form H_2O, while the oxalate ion concentration increases, which is the reverse of the reaction above.   A point is reached where $[Ca^{++}] \times [C_2O_4^=] > K_{CaC_2O_4}$ and calcium oxalate precipitates out.   The solution at this stage is distinctly acid (pH about 4.0) and remains so until most of the calcium has been precipitated out as calcium oxalate. The remaining calcium precipitates out when the solution reacts alkaline.   This removal of most of the calcium in acid solution reduces the co-precipitation of magnesium oxalate and at the same time gives a coarse crystalline precipitate which is easily filtered and washed.

If magnesium is present in excess of the calcium, the calcium is incompletely precipitated unless an excess of oxalate ion is present. Too great excess of oxalate is detrimental because it favors the co-precipitation of magnesium oxalate.   The incomplete precipitation of calcium, when much magnesium is present, is probably due to the formation of a magnesium oxalate complex.   The oxalate ions, as soon as they are added, are removed to form this complex until the necessary equilibrium conditions are satisfied.   At no time during this stage will the concentration of oxalate ion be sufficient to exceed the solubility product of calcium oxalate.   The amount of oxalate added might appear to the analyst as more than enough to precipitate the calcium from solution, an assumption which would probably be true if magnesium were absent.   However, a large part of the oxalate designed to precipitate the calcium will have been removed to form the magnesium oxalate complex and, therefore, it is important to add sufficient oxalate to take care of the formation of the magnesium oxalate complex.

When magnesium is present, the addition of ammonium hydroxide may cause magnesium hydroxide to precipitate. This can be prevented by having present a concentration of ammonium ion sufficient to repress the hydroxyl ion to such an extent that the solubility product of magnesium hydroxide will not be exceeded.   A concentration of NH_4^+ of about 0.1 M is usually sufficient.

236. Filtration and Washing of Calcium Oxalate. — The calcium-oxalate precipitate is filtered through filter paper and is

washed with 0.01 M ammonium-hydroxide solution until free of
chlorides.   In washing calcium oxalate, it is to be noted that this
precipitate shows a marked tendency to creep up the sides of the
filter paper with the result that some of it reaches the top edge of
the filter and is later washed down on the under side of the paper.
With ordinary amounts of calcium oxalate and a 12 cm. filter paper,
as much as 1.0–2.0 mg. of the precipitate may pass into the
filtrate.

   237. Conversion of Calcium Oxalate to Calcium Oxide. — The
calcium oxalate is not weighed as such because the composition is
not uniform.   It is mainly $CaC_2O_4 \cdot H_2O$.   This compound, on
drying, loses water incompletely, and, at 200°, it begins to de-
compose into $CaCO_3$ and CO.   This decomposition proceeds
slowly and is complete at about 400°.   The decomposition of the
oxalate into carbonate and weighing it as such is sometimes recom-
mended, but it is preferable by far to carry the decomposition to
the oxide, which takes place at about 850°, and to weigh it as such.
The reaction involved is

$$CaC_2O_4 \rightarrow CaO + CO + CO_2.$$

By this method a close check upon the decomposition temperature
is unnecessary.   The drawback to weighing the precipitate as oxide
is that the oxide takes on water and CO_2 from the air very rapidly
and also probably occludes gases.   In order to reduce this source
of error to a minimum, the calcium oxide is kept covered during
the cooling and weighing period, and the weighing is conducted
immediately after the cooling.   If a platinum crucible is used for
the ignition of calcium oxalate, the decomposition to oxide is quick
and satisfactory.   If porcelain is used, the decomposition to oxide
is slow and not so satisfactory, especially if the amount of calcium
oxalate is large.

   The determination of calcium by precipitating as oxalate, ignit-
ing in a platinum crucible, and weighing as CaO is suitable for
amounts of calcium equivalent to from 0.0003–0.400 g. of CaO.
As to the precision of the method, it may be stated to be good to 2
parts per 1,000 with quantities in the neighborhood of 0.150 g. of
calcium oxide.   This precision, of course, decreases with de-
creasing amounts of calcium oxide.

238. Conversion of Calcium Oxide to Calcium Sulfate. — When a porcelain crucible is used in converting the calcium oxalate to calcium oxide, it is often desirable to convert the oxide to sulfate and to weigh as calcium sulfate. In order to accomplish this, the ignited precipitate after cooling is carefully treated by adding 9 M sulfuric acid dropwise until it is in excess, and then removing the excess of sulfuric acid by heating in an air bath (§ 20) at about 300°. The dry precipitate is then ignited at a dull red heat for a short time and weighed. The treatment with acid, etc., is repeated until constant weight is obtained.

239. Exercise No. 19. Determination of Calcium Oxide in a Sample of Calcium Carbonate.[1]— Dissolve a half gram of the sample in a covered beaker by means of the cautious addition of 3 M hydrochloric acid. Rinse off the watch-glass when the sample has completely dissolved and dilute the solution to a volume of 200 ml. Heat to the boiling point and add slightly more than sufficient oxalic acid or 0.25 M ammonium oxalate solution to precipitate all the calcium. Now add slowly drop by drop 3 M ammonium hydroxide solution until the solution is alkaline. Allow the precipitate to digest for an hour, filter through a 12 cm. filter paper and wash with 0.01 M ammonium hydroxide solution until free of chlorides. Place the moist precipitate of calcium oxalate (wrapped in the filter paper) in a platinum crucible (which has been weighed with its cover) and heat so as to char without inflaming the paper. When the carbon has been made to disappear by stronger heat and free access of air, cover the crucible and ignite with the full flame of a Meker burner for 15–20 minutes. It is a mistaken idea that it takes a long time to reach constant weight at temperatures of 1,000° or over; even at the temperature of a large and good Bunsen burner (800°) 30 minutes is ample for any amount of lime that is likely to be met with — all this, of course, with the crucible covered. After ignition, place the crucible (with its cover on) in a desiccator for 20 minutes and weigh at once (with cover). Repeat ignition and weighing until consecutive weighings do not differ by more than 0.2 mg. Calculate the percentage of calcium carbonate in the sample or, if desired, express the calcium content of the sample in terms of per cent of CaO.

[1] A good grade of "Analyzed" reagent will answer admirably for this purpose.

240. Determination of Magnesium. — The determination of magnesium is almost invariably based upon the principle of precipitating magnesium ion as magnesium ammonium phosphate by means of di-sodium phosphate from a solution which contains ammonium ion and which is finally made alkaline with ammonium hydroxide. If the precipitate obtained consists of a mixture of $MgNH_4PO_4 \cdot 6H_2O$ and $MgNH_4PO_4 \cdot H_2O$, it must be ignited to $Mg_2P_2O_7$ before weighing. Since $MgNH_4PO_4 \cdot 6H_2O$ is no more difficult to obtain than this mixture of hydrates, and since it may be ignited to $Mg_2P_2O_7$, it is preferable to precipitate magnesium as $MgNH_4PO_4 \cdot 6H_2O$.

The problem of obtaining a precipitate of the desired composition is much the same as that encountered in the determination of phosphorus. The theory involved has already been, discussed in §§ 224–226. It should be reviewed at this juncture and adapted to the determination of magnesium.

In the precipitation of either of the forms of magnesium ammonium phosphate, care must be taken that the solution is free of all forms of silicic acid, likewise from all ions that give insoluble phosphates, namely, ions of the copper, iron and aluminum groups, also from calcium and barium ions.

241. *Summary of Conditions for the Determination of Magnesium.* — The sample to be analyzed should not contain more than 0.100 g. of magnesium, calcium, barium, or strontium; members of the iron group and the heavy metals must be absent. The final volume of the solution must not be over 75 ml. The temperature of the solution must not be over 35°. Ammonium chloride must be present to prevent the precipitation of magnesium hydroxide, but its concentration should not be over 0.4 M. If, in the course of the analysis, there has been an excessive accumulation of ammonium chloride, it must be removed by adding 60 ml. of 16 M HNO_3, evaporating to a small volume over a small flame, adding more nitric acid and again evaporating to incipient dryness. The volume of the solution should then be brought to about 50 ml. Five to six milliliters of 3 M HCl is added and the solution is made slightly alkaline with 3 M NH_4OH. If a precipitate of magnesium hydroxide forms, it must be dissolved by adding 3 M HCl. The solution is again made alkaline with ammonia. This operation is

repeated until the solution is perfectly clear when ammoniacal. The solution is then made acid to methyl orange by adding 3 M HCl. A solution of 0.25 M Na_2HPO_4 is added until present in 40% excess. The amount of disodium hydrogen phosphate solution required is estimated with the aid of the relationship: 1 ml. of 0.1 M $Na_2HPO_4 \equiv 0.0024$ g. Mg $\equiv 0.0040$ g. MgO. Fifteen M NH_4OH is then added dropwise from a burette, with constant stirring, until the solution is alkaline. Additional NH_4OH is added so as to make the final concentration of ammonium hydroxide equal to 1.5 M. The solution is allowed to stand at room temperature (18°–30°) for two hours. The precipitate may then be filtered off on a Gooch crucible, and, following the technique of § 225, washed successively with 1.5 M NH_4OH, 95% alcohol, and ether, sucked dry at the pump for 10 minutes, allowed to stand around in the air for 15–20 minutes, or placed in a desiccator for a no greater length of time and then weighed at once as $MgNH_4PO_4 \cdot 6 H_2O$. The precipitate may also be washed with only 1.5 M ammonium hydroxide and may then be ignited to $Mg_2P_2O_7$. An alternative procedure is to collect the precipitate on filter paper and ignite in a platinum crucible, the cautions mentioned in § 226 being observed.

Limits of Method. Precision.—The method is suitable for samples containing from 0.0004 to 0.120 g. Mg. With respect to the precision, it may be said that, of all the commonly occurring elements, it is probable that the determination of magnesium is attended with the greatest error, and in this regard it is pertinent to quote the authority of Hillebrand[2] who says, "Experience has shown that most analysts are prone to make a very serious plus error in determining moderate amounts of magnesia, such as are found in limestones and Portland cements." All things considered, it is doubtful whether we can claim a precision greater than 5 parts per 1,000 for quantities equivalent to 0.100 g. of magnesium or thereabouts; this precision falls off rapidly with decreasing amounts of magnesium.

242. Determination of Magnesium by Precipitation with 8-hydroxyquinoline. — Magnesium is quantitatively precipitated as magnesium oxyquinolate by 8-hydroxyquinoline from solutions

[2] W. F. Hillebrand, p. 153 of reference given in § 11.

having a pH between 9.5 and 12.5. The structural formula of 8-hydroxyquinoline is
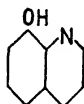
The reaction taking place with Mg^{++} is as follows:

$$Mg^{++} + 2\ HOC_9H_6N + 2\ OH^- \rightarrow Mg(OC_9H_6N)_2 \cdot 2\ H_2O.$$
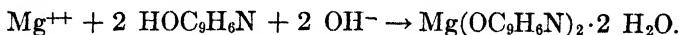
Most metals, with the notable exception of the alkali metals, either form slightly soluble oxyquinolatates or co-precipitate with magnesium oxyquinolate. Such metals, if present, must be removed prior to the determination of magnesium.

Procedure.[3]—The solution from which all interfering ions have been removed and containing less than 50 mg. of magnesium is made neutral to methyl red by adding, if necessary, either hydrochloric acid or ammonium hydroxide. The volume is then brought to 350 ml. and the solution is heated to 60°–70°. The precipitant used in this determination is a 0.0086 M solution of 8-hydroxyquinoline, made by dissolving 12.5 g. of the substance in 30 ml. of glacial acetic acid and diluting to one liter. The precipitant is slowly added until in slight excess as indicated by a permanent yellow color. Ammonium hydroxide is then added, 4 ml. being added for each 100 ml. of solution. The solution is then stirred for 10 minutes, whereupon the precipitate is allowed to settle. The precipitate is collected in a porous bottom crucible, washed with 0.3 M NH_4OH, dried to constant weight at 130°–140° and weighed as $Mg(OC_9H_6N)_2$.

243. Exercise No. 20. Determination of Magnesium and Sulfate in an Unknown Sample. — Determine the percentage of magnesium and sulfate (SO_4) in a sample of crystallized magnesium sulfate $MgSO_4 \cdot 7\ H_2O$; or in a standard solution of it furnished by the instructor.

244. Analysis of Carbonate Rock. — Carbonate rocks, the main constituents of which are calcium carbonate and magnesium carbonate, are very important technically because they serve as raw material for many branches of chemical technology. Such rocks

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[3] Redmond and Bright, *Bur. Standards J. Research*, **6**, 113 (1931).

are classified on the basis of the relative percentages of their content of calcium carbonate and magnesium carbonate. The classification given in Table 39 is somewhat arbitrary, since one group passes into the other by insensible gradations of the relative proportions of the two constituents.

Table 39

CLASSIFICATION OF LIMESTONE

	Limestones	Magnesian or Dolomitic Limestones	Dolomites
% $CaCO_3$.......	96–98	70–93	54–70
% $MgCO_3$......	1–2	5–18	18–46

Besides the major constituents just mentioned, the following minor constituents are almost invariably present in small amounts: The carbonates of iron and manganese, alumina and silica in the form of clay, also iron pyrites (FeS_2) and sometimes a little gypsum ($CaSO_4 \cdot 2\,H_2O$). See Table 67, Chapter XXIII.

For technical purposes, it is seldom considered necessary to analyze carbonate rocks with the same precise detail that is required for geologic purposes, but rather to make the analyses with regard to the technical utilization of the materials[4] and with determination of only the more important constituents. The following constituents are generally all that are required:

> Loss on drying at 104°–110°
> Loss on ignition
> Silica (SiO_2)
> Combined oxides (Fe_2O_3, Al_2O_3, Mn_3O_4, P_2O_5)
> Iron in combined oxides
> Lime (CaO)
> Magnesia (MgO)
> Insoluble matter
> Carbon dioxide

[4] A. S. T. M. Standards, Part II, 51, American Society for Testing Materials, Philadelphia, 1936.

245. Exercise No. 21. Analysis of a Dolomitic Limestone. —
The determination of those constituents listed in the preceding
paragraph will be considered in this analysis.

246. *Loss on Drying at 105°-110°.* — Place about 4 g. of
the pulverized sample in a small evaporating dish which has pre-
viously been dried to constant weight at 105°–110°. Weigh the
dish and contents and dry to constant weight, at 105°–110°, in the
constant temperature oven. Calculate the per cent loss in weight
on drying.

247. *Loss on Ignition.* — The loss on ignition is mainly due to
loss of CO_2 and H_2O. When organic matter is present, its de-
composition may contribute slightly to this loss. The oxidation
of sulfides to sulfates, and of ferrous iron to ferric oxide, would tend
to cause a slight increase in weight. The net result of these effects
is known as the *Loss on Ignition.*

The sample to be analyzed must be finely powdered and must
have been previously dried to constant weight at 105°–110°. The
sample from which the *Loss of Weight on Drying* has been obtained
may be used here. Ignite a platinum crucible and cover to constant
weight, and place about 1 g. of the dried sample in the crucible.
With the cover removed, heat gently at first and then with the
Meker burner or blast lamp. Continue the heating for about 30
minutes and, with the crucible covered, cool in the desiccator and
weigh. Repeat the procedure of igniting, cooling, and weighing
until constant weight is obtained. Calculate the per cent of loss
of weight of the sample.

248. *Removal and Determination of Silica.* — Silica may be
determined from the residue from the *Loss on Ignition* determina-
tion, or, in the event that *Loss on Ignition* is not required, it can be
determined from the dried rock powder.

Add to the residue from the *Loss on Ignition* determination,
or to the dried rock powder, an equal weight of anhydrous sodium
carbonate and ignite at first carefully over a Bunsen flame and
finally over a Meker burner. When the sample is low in silica,
iron and alumina, and high in calcium, the sodium carbonate may
be omitted and the dried rock powder may be ignited alone. Al-
low the sintered mass to cool. To the cold crucible add a little
water and allow to stand for a few minutes. If the sintered mass

can now be detached from the crucible, transfer it to a casserole and wash out the crucible, first with hot water and then with 6 M hydrochloric acid.   Wash off the crucible cover in the same manner.   Make the solution in the casserole acid with 6 M hydrochloric acid and evaporate it to dryness on the water-bath.   Place the casserole and residue in an oven set at 115^{δ}–120° for 30–40 minutes in order to dehydrate the silica.   Any salts of the iron and aluminum groups will be more or less in the basic form, and, in order to obtain their solution, treat the dried residue with 20–25 ml. of 6 M hydrochloric acid and digest on the steam bath for 10–20 minutes, and then, but not before, dilute with 80–100 ml. of water prior to filtration.   The filtration should be conducted through filter paper and the siliceous residue washed with 0.1 M hydrochloric acid until free of all salts (test for Fe^{+++} by 0.1 M KCNS).   If silica is to be determined, proceed as directed in § 460.   It should be borne in mind that after driving off the SiF_4 in the determination of silica, a small residue of Fe_2O_3, Al_2O_3, and other oxides may remain in the crucible.   This residue should be set aside in the crucible for further analysis if the metals present in it are to be determined.

249. Determination of Combined Oxides (Fe_2O_3, Al_2O_3, Mn_3O_4, P_2O_5). — To the filtrate obtained above, add a few drops of bromine.   Then boil the solution until all the excess bromine is expelled.   Now add sufficient hydrochloric acid so that the magnesium will not precipitate when the solution is made alkaline with ammonium hydroxide.   Add a few drops of methyl red solution, and then add ammonium hydroxide, first concentrated and finally dilute, until the solution turns yellow.   Bring the solution to the boiling point and keep it there for a few minutes.   Allow the precipitate to settle.   Filter and wash the precipitate two or three times with hot water.   Too long a time must not elapse between the precipitation and filtration, as otherwise calcium and magnesium carbonates might precipitate, due to absorption of carbon dioxide from the air by the ammoniacal solution.   Set aside the filtrate and washings as they are to be subsequently joined with the filtrate and washings from the reprecipitation of the hydroxides.   Transfer the filter paper and its contents to the beaker in which the first precipitation was made and add a little 12 M hy-

drochloric acid.   Break the paper into a pulp by means of a stirring rod.   Add a little water and warm, turning the beaker so that the solution dissolves any hydroxide that may have adhered to the walls.   After the precipitate has dissolved, dilute the solution to about 300 ml. and heat to boiling.   Reprecipitate the combined hydroxides in the same manner as before and wash with 0.01 M NH_4OH containing 0.1 M NH_4NO_3.   It is important to add the wash solution in such a manner that the precipitate will be thoroughly stirred from the bottom of the filter paper.   After washing the precipitate and filter paper free from chloride, combine the filtrate and washings with those obtained in the previous precipitation.   This combined solution now contains all the calcium and magnesium.   Ignite the filter containing the precipitate in the crucible containing the residue which was set aside after the determination of silica.   After the filter has been carefully ignited, subject the residue to the full flame of the Meker burner for about 30 minutes and then cool in the desiccator and weigh.   The ignited precipitate is sometimes reported as *Combined Oxides* without any further work being done upon it.

250. *Determination of Iron in Combined Oxides.* — If it is required to determine the iron in the combined oxides, this residue is treated as described in § 462.

251. *Determination of Calcium Oxide.* — Concentrate the filtrate from the iron and aluminum hydroxide precipitation to a volume of about 200 ml.   Heat to boiling and treat with an amount of 0.25 M ammonium oxalate solution equivalent to all the calcium and magnesium present plus an excess of 10% of this amount. Add ammonium hydroxide in slight excess and allow the solution to stand on the hot-plate or on a water-bath for about an hour, or until the crystals are large enough to be retained by the filter paper.   Decant the solution through a small filter paper leaving as much of the precipitate as possible in the beaker.   Place the beaker containing the precipitate under the funnel and pour a little hot 3 M hydrochloric acid through the filter to dissolve any precipitate which may have been transferred in decanting the solution.   Wash the paper with hot water until the washings show no test for chloride, then heat the calcium oxalate precipitate with enough 3 M hydrochloric acid to effect its solution.   Dilute to about

150 ml. and add 3 M ammonium hydroxide slowly, drop by drop, until the solution is alkaline; then add a few milliliters of 0.25 M ammonium oxalate solution.   Digest and filter as in the first precipitation, washing the precipitate with hot 0.01 M NH$_4$OH, adding a drop of ammonium oxalate solution each time the funnel is filled. Combine the filtrates containing the magnesium and concentrate them by evaporation to a volume of about 100 ml.   Reserve this solution for use in § 252.   Transfer the filter paper and precipitate to a platinum crucible that has been weighed with its cover. Ignite in the usual way, and finally over the Meker burner.   Cool in a desiccator and weigh the calcium oxide quickly, with the cover in place so that the amounts of moisture and carbon dioxide absorbed shall be negligible.   Ignite to constant weight, and calculate the percentage of calcium as CaO.

252. Determination of Magnesium Oxide. — Assuming that the combined filtrate containing the magnesium has been concentrated to a volume of about 100 ml., allow to cool to room temperature.   If ammonium salts are present in such quantity as to crystallize from the solution on cooling, they may be got rid of by adding 20–30 ml. of 16 M nitric acid from time to time during the evaporation and continuing the evaporation to near dryness.   It is preferable to carry out this evaporation in a Phillips assay beaker (§ 19) over a small flame.   Add about 5 ml. of 3 M hydrochloric acid and then 3 M ammonium hydroxide until slightly alkaline. If a precipitate of magnesium forms, repeat the addition of hydrochloric acid and ammonium hydroxide until the solution can be made ammoniacal without the formation of a precipitate.   Make the ammoniacal solution acid to methyl orange with 3 M hydrochloric acid; heat to boiling and add 0.25 M di-sodium phosphate solution until it is present in 40% excess over the amount theoretically demanded by the stoichiometric equation.   Now add dropwise from a burette 15 M ammonium hydroxide until the solution is just ammoniacal, and then enough more to make the final concentration of ammonium hydroxide 1.5 M.   Allow the solution to stand at room temperature for 2 hours, and complete the determination as detailed in § 225 and § 226.

Calculate the percentage of magnesium in the sample of limestone, as MgO.

253. *Determination of Magnesium as Magnesium Oxyquinolate.* — The alternative method of determining magnesium as the oxyquinolate may be used in the analysis of limestone. The details are given in § 242.

254. *Insoluble Matter.* — The *Insoluble Matter* is determined from the residue after the ignition of the dried rock powder. Transfer the ignited sample to a beaker and add 50 ml. of water. Add 2 M hydrochloric acid until further addition of acid causes no appreciable solution of the sample. Boil for 5 minutes and filter. Wash with water and ignite to constant weight. Calculate the per cent of *Insoluble Matter* in the dried sample.

If the insoluble residue is to be analyzed separately from the soluble portion of the sample, it may be fused with anhydrous sodium carbonate. The fusion is then decomposed with hydrochloric acid and analyzed in the same way as the main portion of the sample obtained by the first treatment with hydrochloric acid.

255. *Carbon Dioxide.* — If it is required to determine carbon dioxide, acid is added to a sample of the limestone. The carbon dioxide evolved is collected in absorption tubes and weighed. The details of this method are given in §§ 452–454.

256. Examples.

1. Calculate the percentage of CO_2 in $CaCO_3$ and in $MgCO_3$. Are these percentages sufficiently different to allow the indirect calculation of Ca and Mg in a mixture of their carbonates?

2. A 1.008 g. sample of limestone was analyzed for its content of Fe_2O_3 and MgO. The following results were obtained, $Mg_2P_2O_7$ 0.0377 g., Fe_2O_3 0.0065 g. What were the percentages of the constituents mentioned? Ans. Fe_2O_3 0.64%. MgO 1.35%.

CHAPTER XIII

DETERMINATION OF ZINC GRAVIMETRICALLY AND VOLUMETRICALLY

257. General Considerations. — There are several methods in use for the determination of zinc.[1] (1) It can be determined gravimetrically by precipitating it as zinc sulfide, converting the zinc sulfide to zinc sulfate and weighing the latter; (2) it can be determined by precipitating it as zinc ammonium phosphate monohydrate, converting the monohydrate to the anhydrous salt by drying it at 100°–105° and weighing the anhydrous salt; (3) it can also be determined volumetrically by precipitating it as zinc potassium ferrocyanide, $Zn_3K_2[Fe(CN)_6]_2$, using either uranyl acetate or uranyl nitrate as an outside indicator, or using either diphenylamine or diphenylbenzidine as an oxidation-reduction indicator.

With respect to the precision of these methods, the first is the most precise, the second less so, and the third least of all. With respect to the amounts of zinc that can be handled by these methods, the first can be used for quantities ranging from 2 to 200 mg. figured as Zn, the second for quantities from 20 to 200 mg., while the third is at its best advantage for quantities between 100 and 200 mg.

Each of the methods mentioned above for the determination of zinc requires the absence of certain elements and permits of the presence of others. For convenience the conditions which must be observed with respect to interfering and non-interfering elements are summarized below in Table 40.

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[1] The precise determination of zinc is not an easy matter. The reader is referred to § 59 which gives a summary of the report of the Committee on Uniformity in Technical Analysts, *J. Am. Chem. Soc.*, **26**, 1648 (1904). Their report showed results from forty-two analysts ranging from 12.20% to 39.22% on a sample of zinc ore containing 18.16% of zinc.

Table 40

Summary of Interfering and Non-interfering Substances
in the Precipitation of Zinc

Precipitation of Zinc as	Requires Absence of	Allows Presence of
ZnS	Silicic acid, cobalt and those metals whose sulfides have a smaller solubility product than that of zinc sulfide, that is, members of the copper, tin and silver groups.	Iron, aluminum, nickel and manganese; members of the alkali and alkaline earth groups.
$ZnNH_4PO_4 \cdot H_2O$	Silicic acid, potassium and almost every metal of the alkaline earth and the other groups because of the insolubility of their phosphates.	Only ammonium and sodium salts and the latter in small quantities only.
$Zn_3K_2[Fe(CN)_6]_2$	Silicic acid and practically all metals of the alkaline earth and other groups (except as noted) because of the insolubility of their ferrocyanides.	Aluminum and lead in small quantities and members of the alkali group.

258. Separation of Interfering Substances. — Regardless of which of the foregoing methods is to be used for the determination of zinc, the following sequence gives the general order of procedure that must be observed in the removal of the interfering substances: (1) silicic acid, (2) copper, (3) remaining metals of the copper and tin groups, (4) members of the iron and alkaline earth groups. With respect to the handling of these several groups, particularly the iron group, it is to be remarked that many shortened methods of separation are possible, depending on the absence of certain of the interfering substances. For such methods the student is referred to works on technical analysis, such as Griffin, Lord and Demorest, etc., the references to which are given in § 11. The scheme of procedure presented in the following paragraphs[2] is

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[2] Essentially this scheme is that due to Waring, *J. Am. Chem. Soc.*, **29, 265** (1907).

offered not alone because of its general applicability but because it isolates the zinc in the form of zinc sulfide, thereby allowing the student the option of the determination of the zinc by any of the above three methods which he or the instructor may elect.

Silicic acid will generally only be encountered in the case of ores. It is best got rid of by adding about 20 ml. of 9 M sulfuric acid to the solution of the sample and evaporating it in a casserole until copious fumes of sulfur trioxide have come off for five minutes or so. The solution is allowed to cool, carefully diluted with 40–50 ml. of water, then heated to dissolve any basic salts. It is next filtered while hot and the filter paper washed with hot water. The filtrate can be used at once for the removal of copper if this element is present.

Unfortunately, copper must not be precipitated as copper sulfide in the presence of zinc ion because copper sulfide will invariably drag down zinc even though the solubility product of zinc sulfide is not reached (§ 190). This dragging down will happen even if the copper sulfide is precipitated from a solution which contains as high a concentration of hydrogen ion as corresponds to 1 M hydrochloric acid. Therefore, when copper is present in the determination of zinc, it must be removed either by electrolysis or by electro-deposition with metallic aluminum. The conditions for the former method will be found in § 416; for the latter method it is necessary that *all traces of nitric and hydrochloric acids be absent* and that the solution have a concentration of free sulfuric acid of about 1.5 M. A piece of heavy sheet aluminum about 3 cm. square and bent up at its corners is introduced into the solution, which should have a volume of about 100 ml., and the solution is boiled for ten minutes or until complete reduction of the copper has been effected. The solution is then immediately filtered through a filter paper in which is placed a small piece of the aluminum sheet in order to redeposit any copper that may have become dissolved, and the filter paper is then washed with hot water.

The action of metallic aluminum in the presence of 1.5–2.0 M sulfuric acid at boiling temperature results in the reduction of the following ions to metal:

Lead (Pb^{++})

Copper (Cu^{++} and Cu$^+$)

Arsenic (As^{+++} only; AsO$_4^{\equiv}$ and As^{+++++} are slowly reduced to As^{+++})

Antimony (Sb^{+++})

Tin (Sn^{++++} and Sn^{++})

Cobalt (Co^{++})

Nickel (Ni^{++})

Cadmium and bismuth are only partially reduced, so that if present they will be found in the filtrate from the deposition and must be precipitated by hydrogen sulfide along with any pentavalent arsenic that may be present. It is to be noted in this connection that cadmium sulfide, like copper sulfide, drags down zinc sulfide, but upon solution of the cadmium sulfide and reprecipitation, the amount of zinc which is dragged down the second time is negligibly small.

The proper acidity for the hydrogen sulfide precipitation is that obtained by making the solution 0.3 M with respect to hydrochloric acid. This is the same acidity that applies in general for the

Table 41

MAXIMUM ACIDITIES FOR QUANTITATIVE PRECIPITATION OF SULFIDES

Maximum Acidity	12 M HCl	7.5 M HCl		3.7 M HCl	2.5 M HCl		0.7 M HCl
Element.........	As	Hg	Cu	Sb	Bi	Sn^{++++}	Cd
Maximum Acidity	0.31M HCl	pH = 1.9		pH = 3.		pH = 4.	
Element.........	Pb. Sn^{++}	Zn		Co	Ni	Fe^{++} Mn	

separation of the tin and copper group from the iron and aluminum group. If the acidity is much greater than this, some lead and some tin will remain in solution; while, if the acidity is much less, some zinc sulfide will be precipitated by virtue of its solubility product being exceeded. The behavior of the several elements with respect to their sulfides is shown in Table 41, where the ele-

ments are arranged in descending order of the maximum acidity allowable for the quantitative precipitation of their sulfides.[3]

259. Precipitation of Zinc Sulfide. — After the insoluble sulfides of the tin and copper groups have been filtered off, the filtrate can be used for the separation of the zinc from cobalt,[4] nickel, iron and maganese by precipitating the zinc as sulfide after the acidity has been adjusted to a value of pH = 2.1. The procedure is as follows: The filtrate from the hydrogen sulfide precipitation of the copper and tin groups (copper having been previously removed by electrolysis or electro-deposition) is evaporated to a volume of 125 ml. if the volume is greater than this amount. It is then freed of hydrogen sulfide by boiling in a 750 ml. Erlenmeyer flask until the escaping steam no longer smells of hydrogen sulfide; the solution is cooled to room temperature and 6 M ammonium hydroxide is added until the precipitate which first forms just fails to redissolve. 25 ml. of 1 M citric acid (200 g. citric acid per liter) are added, also a few drops of methyl orange indicator, and then 6 M ammonium hydroxide until the solution is neutral to the methyl orange. If the solution has not been previously cooled, the methyl orange will be rapidly destroyed by the hot solution and its use would be unreliable. The prior removal of the hydrogen sulfide is also essential, as this agent destroys methyl orange. 25 ml. of "formic mixture" is next added, then 20 ml. of 24 M formic acid, after which the volume of the solution is made up to 200 ml. This procedure is necessary in order to establish the right concentration of hydrogen ion for the precipitation and at the same time to provide a buffer to hold the concentration of hydrogen ion sensibly constant during the process of precipitation (see § 127).

"Formic mixture" is a solution of the following composition: 200 ml. of 24 M formic acid (sp. gr. 1.20), 30 ml. of 15 M ammonium hydroxide, and 200 g. of ammonium sulfate, made up to one liter with distilled water. The function of the ammonium sulfate is to

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[3] The data for the copper and tin group are taken from the work of Noyes and Bray, *J. Am. Chem. Soc.*, **29**, 137 (1907); that for the iron group are arrived at from a consideration of the solubility product, § 179; and the work of Fales and Ware, *J. Am. Chem. Soc.*, **41**, 487 (1919).

[4] The amount of cobalt must not exceed one-sixth the weight of the zinc present.

aid in "salting out" the zinc sulfide in granular form as recommended by Treadwell in accordance with the work of G. H. Kramers who also showed that ammonium chloride or thiocyanate are equally good for this purpose.   Since zinc is usually precipitated as the sulfide from a sulfate solution in the analysis of an alloy or ore, the choice of ammonium sulfate seems to be the preferable one for the "salting out" effect.

The flask containing the solution being analyzed is placed on a wire gauze supported on a tripod and heated to about 60°–70°. Then a two-hole rubber stopper, having each hole fitted with a glass tube which is bent at right angles and which just passes through the stopper, is placed snugly and securely in the neck of the flask.   One of the bent glass tubes is connected by means of a piece of rubber tubing to a wash bottle which contains distilled water and is connected in turn with a hydrogen sulfide generator; the other glass tube is equipped with a short piece of rubber tubing to be subsequently closed by means of a pinch clamp.   After having introduced the rubber stopper and having observed that the exit tube is *open* the hydrogen sulfide is allowed to flow so as to displace the air in the flask and the heating is continued until the solution almost boils.   The burner is removed and the exit tube is closed with a pinch clamp at once, but the hydrogen sulfide supply is kept open and connected with the precipitation flask.   The latter is shaken frequently to insure complete saturation.   When the solution has cooled to 25°–30°, the supply of hydrogen sulfide may be turned off.   The precipitate of zinc sulfide, which should be white in color, will usually settle within thirty or forty minutes and will be ready for filtration.   It often happens, in the process of precipitation, especially when the flask has not been thoroughly cleaned, that a layer of zinc sulfide sticks so firmly to the sides of the flask that it cannot be removed.   The precipitate adhering to the flask is then dissolved in hot dilute sulfuric acid (2–3 ml. of 18 M sulfuric acid in 25 ml. of water), just neutralized with ammonium hydroxide, or better, neutralized and then made slightly acid with formic acid, saturated with hydrogen sulfide under pressure, heated to boiling to coagulate the precipitate, and filtered through the filter containing the already washed precipitate of zinc sulfide.   Further washing is unnecessary, as any salt or acid present is volatile.

The precipitate of zinc sulfide is filtered through an ashless filter paper and washed thoroughly with 0.1 M formic acid saturated with hydrogen sulfide. The zinc can now be determined by any one of the three methods previously mentioned: Namely, (1) the precipitate can be converted to zinc sulfate and weighed as such; (2) it can be dissolved in hydrochloric acid and the zinc precipitated as zinc ammonium phosphate $ZnNH_4PO_4 \cdot H_2O$, which is converted to $ZnNH_4PO_4$ by drying to constant weight at $100°–105°$; (3) it can be dissolved in hydrochloric acid and the zinc determined volumetrically by precipitation as the double zinc potassium ferrocyanide $Zn_3K_2[Fe(CN)_6]_2$, using uranyl acetate or diphenylamine as the indicator. Before passing on to the details of these several methods, however, it will be advantageous to discuss the theory involved in the precipitation of zinc as sulfide. Should the reader wish to omit this theoretical discussion for practical considerations, he should proceed directly to § 262.

260. Theory of Precipitation of Zinc as Sulfide. — When any zinc salt in which the anion is that of a strong acid, such as sulfuric acid, hydrochloric acid, etc., is dissolved in water and the zinc precipitated as zinc sulfide, there results an increase of the hydrogen ion concentration of the solution, thus,

$$Zn^{++} + H_2S \rightarrow ZnS + 2H^+.$$
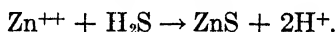
The actual change in hydrogen ion concentration due to the above reaction is shown in Table 42. The solution used for precipitation

Table 42

CHANGE IN HYDROGEN ION CONCENTRATION DURING PRECIPITATION OF ZINC SULFIDE

No.	Initial[5] Conc. H^+	Final Conc. H^+
1.................	$10^{-3.90}$	$10^{-1.86}$
2	$10^{-3.93}$	$10^{-1.86}$

[5] The electromotive force method was used for the measurement of the hydrogen ion concentration with the following combination:

Hg | HgCl, sat. KCl | sat. KCl | H^+ | Pt, H_2
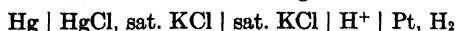
in which all measurements were made at the temperature of $25°$. The value of the pole potential difference Hg | HgCl, sat. KCl, for this temperature, has been taken as 0.249 volt.

contained 1 g. of zinc ammonium sulfate $Zn(NH_4)_2(SO_4)_2 \cdot 6\ H_2O$ in a volume of 200 ml. With the increase in the hydrogen ion concentration there is a decrease in the sulfide ion concentration because of the equilibrium that exists between hydrogen ion, sulfide ion and undissociated hydrogen sulfide, namely,

$$\frac{[H^+]^2[S^=]}{[H_2S]} = 1 \times 10^{-22}.$$

For saturated solutions of H_2S containing varying concentrations of hydrogen ion, the total concentration of H_2S is sensibly 0.1 M. Since the extent of ionization of the H_2S is extremely small, the concentration of un-ionized H_2S is substantially 0.1 M. For such solutions, the relationship between hydrogen ion concentration and sulfide ion concentration is shown in Table 43.

Table 43

HYDROGEN ION AND SULFIDE ION CONCENTRATIONS IN SOLUTIONS
SATURATED WITH HYDROGEN SULFIDE

Solution Saturated with H_2S	$[H^+]$	$[S^=]$
Water	10^{-4}	10^{-15}
0.001 M H^+	10^{-3}	10^{-17}
0.01 M H^+	10^{-2}	10^{-19}
0.1 M H^+	10^{-1}	10^{-21}
0.3 M H^+	$10^{-0.7}$	$10^{-20\ 6}$

Now it so happens that the solubility product of zinc sulfide has such a value, namely,

$$[Zn^{++}]\ [S^=] = 10^{-23}$$

that for the concentrations of zinc ion met with in quantitative analysis, zinc will not be quantitatively precipitated if the concentration of hydrogen ion becomes greater than $10^{-1.90}$. This fact is shown by the following series of experiments where in each experiment the amount of zinc ammonium sulfate hexahydrate was 1.000 g., the volume of the solution was 200 ml., and the acidity and composition of the solution were as noted. The zinc was precipitated as zinc sulfide, transposed to the sulfate and weighed as $ZnSO_4$.

Table 44

INCOMPLETENESS OF PRECIPITATION OF ZINC SULFIDE AS A FUNCTION OF THE
CONCENTRATION OF HYDROGEN ION

a. Sulfuric Acid.   Volume of Solution in Each Case = 200 ml.

No.	Molarity H_2SO_4	Initial Conc. H^+	Sample $Zn(NH_4)_2 -$ $(SO_4)_2 \cdot 6H_2O$ g.	ZnSO₄ Added g.	ZnSO₄ Found g.	Average Error Parts per 1,000
1	0.050	$10^{-1.22}$	1.0004	0.4021	0.3642	121
	0.050	$10^{-1.29}$	0.9999	0.4019	0.3431	
2	0.037	$10^{-1.36}$	1.0010	0.4023	0.3721	79
	0.037	$10^{-1.31}$	1.0005	0.4021	0.3688	
3	0.025	$10^{-1.45}$	1.0009	0.4023	0.3975	10
	0.025	$10^{-1.46}$	1.0009	0.4023	0.3989	
4	0.005	$10^{-1.81}$	1.0008	0.4022	0.4012	4
	0.005	$10^{-1.90}$	1.0002	0.4020	0.3999	

b. Formic Acid + Formic Mixture.   Volume of Solution = 200 ml.

No.	Formic Acid ml.	Formic Mixture ml.	Initial Conc. H^+	Sample $Zn(NH_4)_2 -$ $(SO_4)_2 \cdot 6H_2O$ g.	ZnSO₄ Added g.	ZnSO₄ Found g.	Average Error Parts per 1,000
5	45	25	$10^{-1.61}$	1.0012	0.4024	0.4017	2
6	35	25	$10^{-1.84}$	0.9997	0.4018	0.4009	2
7	20	25	$10^{-2.16}$	1.0008	0.4022	0.4022	1
	20	25	$10^{-2.08}$	1.0007	0.4022	0.4013	
8	10	25	$10^{-2.45}$	1.0008	0.4022	0.4015	1
	10	25	$10^{-2.45}$	1.0009	0.4023	0.4021	
9	..	25	$10^{-2.97}$	1.0008	0.4022	0.4021	1
		25	$10^{-3.02}$	0.9997	0.4018	0.4012	

c. Formic Acid + Ammonium Formate + Ammonium Sulfate

No.	Formic Acid ml.	Ammonium Formate g.	Ammonium Sulfate g.	Initial Conc. H^+	Sample $Zn(NH_4)_2$ $(SO_4)_2 \cdot 6H_2O$ g.	ZnSO₄ Added g.	ZnSO₄ Found g.	Average Error Parts per 1,000
10	10	0.70	6.25	$10^{-3.19}$	1.0000	0.4019	0.4014	1
	10	0.70	6.25	$10^{-3.10}$	1.0006	0.4021	0.4023	
11	1	0.70	6.25	$10^{-3.98}$	1.0000	0.4019	0.4013	2

The results given in Table 44 are portrayed graphically in Figure 52 where it is easily seen that the best range of hydrogen ion for the quantitative precipitation of zinc sulfide is between 10^{-2} and 10^{-3}. With concentrations of hydrogen ion greater than 10^{-2}, the completeness of precipitation falls off rapidly, while with concentrations less than 10^{-4}, although zinc is still quantitatively precipitated, it tends to come down in a slimy form which is difficult to filter.[6]
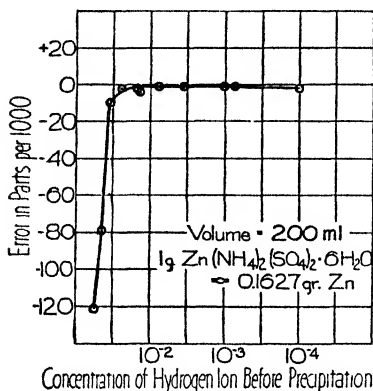
Fig. 52

Incompleteness of Precipitation of Zinc Sulfide as a Function of the Hydrogen Ion Concentration

261. Precipitation of Zinc in the Presence of Cobalt, Nickel, Iron and Manganese.— When elements of the iron group, *i.e.*, cobalt, nickel, iron and manganese are present, it is better to work at a concentration of hydrogen ion as near $10^{-2.0}$ as possible, as this lessens the chances of exceeding the solubility products of the sulfides of these elements although allowing a quantitative precipitation of the zinc sulfide. This concentration of hydrogen ion is provided by the use of 25 ml. of formic mixture $+$ 20 ml. of 24 M formic acid in a total volume of 200 ml. either in the absence or presence of 25 ml. of molar ammonium citrate, which latter it is

[6] Regions beyond 10^{-4} were not investigated because of the formation of slimy zinc sulfide. Experiments conducted by Glixelli, *Z. anorg. Chem.*, **55**, 306 (1907), show that the precipitate from neutral solutions is 4.6 times as soluble as that from acid solutions, the difference in solubility being attributed to the difference in size of the grains. There is also some evidence that zinc sulfide, first precipitated from solutions alkaline with ammonium hydroxide, dissolves in the presence of excess of hydrogen sulfide, a result similar to that reported by McCay for solutions alkaline with sodium or potassium hydroxide. *J. Am. Chem. Soc.*, **30**, 376 (1908).

necessary to use whenever elements of the iron group are present in order to help hold them up as complex citrates.[7]

The buffer action of the formic mixture is shown by the experimental results given in Table 45 and graphically depicted in Figure 53. Varying amounts of this formic mixture were used in a series of experiments where a uniform amount, 1 g. of zinc ammonium sulfate (0.1627 g. zinc), was used, and the total volume of the solution from which the precipitation of zinc sulfide was to be made was kept definitely at 200 ml. each time.

Fig. 53

Buffer Action of Formate Ion in the Precipitation of Zinc Sulfide

The measurement of the hydrogen ion concentration in these solutions gave the values of this factor before precipitation.

Table 45

CHANGE OF HYDROGEN ION CONCENTRATION AS A FUNCTION OF SULFURIC
ACID LIBERATED, USING FORMIC MIXTURE

No.	Formic Mixture ml.	Initial Conc. H^+	Final Conc. H^+
1	0	$10^{-3.90}$	$10^{-1.77}$
2	10	$10^{-2.71}$	$10^{-2.25}$
3	20	$10^{-2.60}$	$10^{-2.35}$
4	30	$10^{-2.62}$	$10^{-2.35}$
5	40	$10^{-2.58}$	$10^{-2.35}$

The same narrow variation in the concentration of hydrogen ion also obtains when ammonium citrate is present.   Thus upon

[7] Spiller, *J. Chem. Soc., London*, **10**, 113 (1857) was apparently the first to notice this effect of the citrate ion in forming complexes with elements of the iron group.

repeating the preceding conditions with the addition of 25 ml. of 1 M ammonium citrate, the results given in Table 46 and portrayed graphically in Figure 54 were obtained.

Table 46

CHANGE OF HYDROGEN ION CONCENTRATION AS A FUNCTION OF SULFURIC ACID LIBERATED, USING 25 ML. 1 M CITRIC ACID + 2.4 ML. 15 M AMMONIUM HYDROXIDE + FORMIC MIXTURE

No.	Formic Mixture ml.	Initial Conc. H$^+$	Final Conc. H$^+$
1	0	$10^{-3.71}$	$10^{-3.39}$
2	10	$10^{-3.19}$	$10^{-2.99}$
3	20	$10^{-2.99}$	$10^{-2.85}$
4	30	....	$10^{-2.78}$
5	40	$10^{-2.86}$	$10^{-2.72}$

The efficacy of separating zinc as zinc sulfide from cobalt, nickel, iron and manganese rests upon the fact that the zinc will be quantitatively precipitated while the others will be negligibly precipitated if the concentration of hydrogen ion is kept at about $10^{-2.4}$ and sufficient ammonium citrate is present. The use of 25 ml. of 1 M ammonium citrate + 25 ml. of formic mixture + 20 ml. of 24 M formic acid in a total volume of 200 ml. will establish the necessary concentration of hydrogen ion by virtue of the formic mixture and the formic acid, while the ammonium citrate will help to hold up the cobalt, nickel, iron and manganese (unless these are present in too great quantity) by vir-
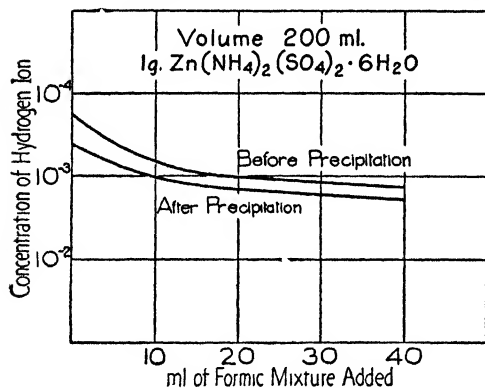
Fig. 54

Buffer Action of Formate Ion in the Presence of Ammonium Citrate, during the Precipitation of Zinc Sulfide

Table 47

PRECIPITATION OF ZINC SULFIDE IN THE PRESENCE OF COBALT, NICKEL, IRON, AND MANGANESE

Separation of Zinc from Cobalt

Sample $Zn(NH_4)_2-$ $(SO_4)_2 \cdot 6H_2O$ g.	Co Added g.	ZnSO$_4$		Diff. g.
		Added g.	Found + impurity g.	
1.0014	0.160	0.4025	0.4251	0.0226

Separation of Zinc from Nickel

Sample $Zn(NH_4)_2-$ $(SO_4)_2 \cdot 6H_2O$ g.	Ni Added g.	ZnSO$_4$		Diff. g.
		Added g.	Found + impurity g.	
1.0001	0.160	0.4019	0.4004	− 0.0015

Separation of Zinc from Varying Amounts of Iron

No.	Sample $Zn(NH_4)_2-$ $(SO_4)_2 \cdot 6H_2O$ g.	Fe Added g.	Fe Found with ZnSO$_4$ Calc. to Fe$_2$(SO$_4$)$_3$ g.	ZnSO$_4$			Diff. g.
				Added g.	Found + impurity g.	Found corrected g.	
1	1.0009	0.032	0.0006	0.4023	0.4025	0.4019	−0.0004
2	1.0005	0.064	0.0008	0.4021	0.4028	0.4020	−0.0001
3	1.0002	0.128	0.0009	0.4020	0.4037	0.4028	+0.0008
4	1.0007	0.160	0.0010	0.4022	0.4027	0.4017	+0.0007
5	1.0008	0.320	0.0026	0.4022	0.4050	0.4024	+0.0004

Separation of Zinc from Varying Amounts of Manganese

No.	Sample $Zn(NH_4)_2-$ $(SO_4)_2 \cdot 6H_2O$ g.	Mn Added g.	Mn Found with ZnSO$_4$ Calc. to MnSO$_4$ g.	ZnSO$_4$			Diff. g.
				Added g.	Found + impurity g.	Found corrected g.	
1	1.0042	0.016	0.00003	0.4036	0.4034	0.4034	−0.0002
2	1.0003	0.032	0.00006	0.4020	0.4018	0.4017	−0.0003
3	1.0003	0.082	0.00006	0.4020	0.4026	0.4025	+0.0005
4	1.0001	0.160	0.00016	0.4019	0.4023	0.4021	+0.0002

tue of complex ion formation. The results obtained under the fore-
going conditions are given above in Table 47 from which it will be
noted that only in the case of cobalt does any appreciable amount
of the interfering element come down[8] while in the case of nickel,
iron and manganese, practically none of these elements come down.

262. Treatment of the Precipitate of Zinc Sulfide. — We will
now resume at the point where we left off at the end of § 259 and
proceed with a discussion of the three methods by which the pre-
cipitate of zinc sulfide can be handled. The choice of which way
to proceed now depends partly upon the option of the analyst and
partly upon the considerations stated in § 257.

263. Conversion of Zinc Sulfide to Zinc Sulfate. — In this
method ZnS is converted to $ZnSO_4$ and weighed. A modification
of the method of Sullivan and Taylor for this conversion has been
chosen for this purpose.[9]

The modification, which is chiefly a time-saving device, con-
sists in the direct treatment of the sulfide with concentrated
sulfuric acid after ignition of the filter paper, thus avoiding the
re-solution of the sulfide in dilute hydrochloric acid and the
evaporation before treatment with sulfuric acid.

The details of procedure are as follows: After the precipitate has
been filtered and washed with 0.1 M formic acid, which is saturated
with hydrogen sulfide, it is transferred to a weighed porcelain
crucible and the filter paper is charred, preferably by standing the
crucible upon a quartz plate, which is heated strongly by means of

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[8] The work of Funk, *Z. anal. Chem.*, **46**, 93 (1907) has shown, however, that
the concentration of hydrogen ion named above, *i.e.*, $10^{-2.1}$ allows a quantita-
tive separation of zinc from one-fifth to one-sixth its weight of cobalt.

[9] *Ind. Eng. Chem.*, **1**, 476 (1909). In the method of Sullivan and Taylor the
precipitate of zinc sulfide is first dissolved in dilute hydrochloric acid, and
boiled to expel excess of hydrogen sulfide, then transferred to a weighed
porcelain crucible, and evaporated on a water-bath with a little more than the
theoretical weight of sulfuric acid required to form zinc sulfate. The crucible
is then heated in an air-bath (§ 20), and finally ignited over a Bunsen burner.
The authors state that the method is accurate to 0.1 or 0.2%.

The experiments of Euler, *Z. anorg. Chem.*, **25**, 146–154 (1900), show that
determination of zinc as the sulfate is comparable with Volhard's sulfate
method for manganese.

Breyer states that the sulfate method is just as accurate as the oxide method.
Report of 8th Internat. Congress of Pure and Applied Chemistry, **25**, 10 (1912).

a Meker burner.[10]   The ignition of the filter paper is very slowly and carefully completed in an oxidizing atmosphere over a Bunsen burner.   The reaction should proceed only to the formation of $ZnSO_4$ and not to ZnO.   If the reaction proceeds to ZnO, the subsequent moistening of the residue with concentrated sulfuric acid often generates heat enough so that the water which is formed according to the reaction, $ZnO + H_2SO_4 \rightarrow H_2O + ZnSO_4$, is converted into steam, and particles of the precipitate are thrown out of the crucible.   After cooling, the precipitate is carefully moistened with a few drops of 9 *M* sulfuric acid, and the crucible is heated in an air-bath until the excess acid is driven off, then heated over the Bunsen burner to remove any charred material.   The precipitate is again moistened with concentrated sulfuric acid and the crucible heated in the air-bath, until the excess of acid is driven off; it is allowed to cool, then weighed; the moistening with sulfuric acid and subsequent evaporation is continued to constant weight, two such treatments usually being sufficient.   A blank is run to correct for any impurities in the reagents, and the residue (usually about 0.2 mg.) is subtracted from the final weight of zinc sulfate.

Precision. — The results given in Table 48 show that the method of precipitating zinc as zinc sulfide, and then converting the sulfide

Table 48

DETERMINATION OF ZINC BY PRECIPITATION AS THE SULFIDE BY THE MODIFIED FORMIC ACID METHOD, WITH CONVERSION TO THE SULFATE

No.	Sample $Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$ g.	$ZnSO_4$		Difference g.
		Added g.	Found g.	
1	1.0484	0.4214	0.4211	−0.0003
2	1.0041	0.4036	0.4036	0.0000
3	1.0645	0.4278	0.4279	+0.0001
4	1.0225	0.4109	0.4106	−0.0003
5	1.0008	0.4022	0.4021	−0.0001
6	0.9997	0.4018	0.4012	−0.0006
				Av. −0.0002

[10] This is a convenient method, in general, for charring filter paper previous to ignition.

to zinc sulfate, is accurate to within 0.5 to 1 part per 1,000 for amounts of zinc equal to 0.160 g.

264. Precipitation as Zinc Ammonium Phosphate. — The zinc sulfide obtained by precipitation with hydrogen sulfide is dissolved through the filter paper [11] into a beaker by means of 25–30 ml. of 6 M hydrochloric acid, and the solution boiled until it is free of hydrogen sulfide. In this method the Zn^{++} is precipitated as $ZnNH_4PO_4 \cdot H_2O$. This precipitate is soluble in acids because of the repression of the concentration of the phosphate ion by the hydrogen ion. It is also soluble in alkalies by virtue of the repression of the zinc ion through formation of the zincate ion. In a similar manner, it is soluble in ammoniacal solutions through formation of the zinc ammonium complex ion. The exact value of pH for which zinc ammonium phosphate is least soluble has not been definitely ascertained, but apparently is close to a pH of 7.5. The preliminary adjustment of the acidity at this juncture is a matter of extreme importance in order to insure the correct value of pH after the addition of the di-ammonium phosphate $(NH_4)_2HPO_4$ which is used as the precipitant. To adjust the pH, the solution is cooled and a drop of methyl orange solution is added. The hydrochloric acid is then neutralized very carefully with ammonium hydroxide. The solution is next diluted to about 150 ml., and heated on a water-bath to about 60° when a solution of di-ammonium hydrogen phosphate $(NII_4)_2HPO_4$ is added in large excess, *i.e.*, about ten times the theoretical amount necessary to combine with the zinc.[12] The heating is continued on the water-bath until the flocculent precipitate of zinc orthophosphate $Zn_3(PO_4)_2$ changes into the crystalline precipitate of zinc ammonium phosphate, $ZnNH_4PO_4 \cdot H_2O$, after which the solution is cooled to room temperature and the precipitate filtered on a Gooch crucible. The precipitate is washed first with 0.1 M di-ammonium phosphate solution and then with cold water, applying a correction of 0.5 mg. Zn for every 100 ml. of water used. It is preferable to dry the precipitate at 100°–105° and weigh as $ZnNH_4PO_4$ rather than to

[11] If the zinc is in the form of a soluble salt to begin with, and the only other substances present are ammonium or sodium salts, and not much of the latter, the prior precipitation of the zinc as zinc sulfide is unnecessary.

[12] 1 ml. 0.1 M $(NH_4)_2HPO_4 \equiv 6.5$ mg. Zn.

attempt its conversion to $Zn_2P_2O_7$ because of the fact that zinc pyrophosphate is appreciably volatile at the temperature necessary for its conversion (full red heat) from zinc ammonium phosphate.

265. Volumetric Determination of Zinc as Zinc Potassium Ferrocyanide. General Considerations. — This method of determining zinc is based on the fact that under certain definitely prescribed conditions of acidity, temperature, etc., zinc ion reacts with ferrocyanide ion in the presence of potassium ion to form the insoluble salt, zinc potassium ferrocyanide, according to the reaction,

$$3\ Zn^{++} + 2K^+ + 2\ Fe(CN)_6^{\equiv} \rightleftharpoons Zn_3K_2[Fe(CN)_6]_2 \downarrow \quad (1)$$
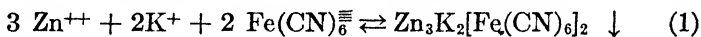
The composition of the precipitate, however, varies more or less with any variation in the conditions which exist during its formation, so that in order to obtain the above equivalence the following conditions must be rigidly observed.[13] The volume of the zinc solution should be 200 ml.; the free hydrochloric acid should be 6 ml. of 12 M HCl; 10 g. of ammonium chloride should be present; the temperature of the solution during the addition of the precipitant should be 70°; and the solution should be about 0.05 M with respect to potassium ferrocyanide (that is 21.6 g. of $K_4Fe(CN)_6 \cdot 3$ H_2O per liter). Metals such as iron, which form insoluble ferrocyanides, must be absent.

As it is not possible to wash the precipitate on account of its gelatinous nature and its bulkiness, nor to dry it to definite composition if it could be washed, its employment rests entirely upon the fact that it furnishes a very satisfactory volumetric method for the determination of zinc when either uranyl nitrate $(UO_2)(NO_3)_2$ or uranyl acetate $(UO_2)(C_2H_3O_2)_2$ is used as an outside indicator, or when diphenylamine or diphenylbenzidine is used as an oxidation-reduction indicator.

266. Titration of Zinc Using Outside Indicator. — In this titration the uranyl ion UO_2^{++} unites with any excess ferrocyanide ion to form the insoluble red-brown uranyl ferrocyanide $(UO_2)_2$ $Fe(CN)_6$, thus,

$$2UO_2^{++} + Fe(CN)_6^{\equiv} \rightarrow (UO_2)_2Fe(CN)_6 \downarrow . \quad (2)$$
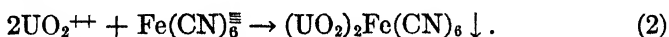
[13] Blasdale, pp. 299–301 of reference cited in § 11, gives an excellent presentation of the variability of this reaction brought about by varying the volume, the concentration of hydrochloric acid, the temperature, etc.

The solubility product of uranyl ferrocyanide is somewhat larger with respect to the solubility product of zinc potassium ferrocyanide than can be desired, so that the end point with a uranyl salt as indicator and 0.05 M potassium ferrocyanide as the titrating agent occurs at about 0.5–0.7 ml. after the stoichiometric point of reaction (1) has been reached. It is, therefore, always necessary to determine the allowance for the end point under conditions parallel to those used in the titration of the zinc.

Allowance for the End Point. — To determine the allowance for the end point, a solution of 0.05 M uranyl acetate or the same strength uranyl nitrate is prepared[14] and 3–4 drops of it are placed in each of the several cavities of a spot-tile. To 200 ml. of water in a beaker, 6 ml. of 12 M hydrochloric acid and about 10 g. of ammonium chloride are added. The solution is then heated to 70°. To the hot solution a drop or two of the standard potassium ferrocyanide solution is added and the solution is stirred vigorously with a clean stirring rod. A drop of the solution is then withdrawn from the beaker by means of the stirring rod and mixed thoroughly with the uranyl acetate or uranyl nitrate indicator in one of the cavities of the spot-tile. This procedure is repeated, employing another cavity each time and taking care that the stirring rod is always wiped clean before being re-used for stirring. Continue this procedure until a drop from the solution in the beaker produces a well-defined brownish tinge within a few seconds after being mixed with the indicator. As this brownish tinge becomes progressively deeper with excess of reagent and with time of standing, it is better not to try to match any permanent color standard but rather to adopt as the end point the first brownish tinge that can be recognized without any hesitancy whatever within the first few seconds after the mixing of the drop from the solution and the contents of one of the cavities. The excess of 0.05 M potassium ferrocyanide necessary to establish the end point under the above conditions, varies from 0.5–0.7 ml.; the exact quantity of potassium ferrocyanide solution must be determined experimentally by the analyst and must be deducted from every titration made.

[14] Uranyl acetate, $UO_2(C_2H_3O_2)_2 \cdot 2H_2O$, mol. wt. 424.3; uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, mol. wt. 502.3.

267. Exercise No. 22. Standardization of Potassium Ferrocyanide Solution. — Owing to the variability of reaction (1) (§ 265) and to the large excess of potassium ferrocyanide solution necessary to establish the end point, it is not sufficiently accurate to dissolve an exact amount of potassium ferrocyanide, make it up to volume and then calculate the value of the solution from the equivalence of reaction (1). The value of the solution, which for convenience should be about 0.05 M (21.6 g. $K_4Fe(CN)_6 \cdot 3\ H_2O$ per liter), must be determined by titration against a known amount of zinc.[15]

Procedure. — Weigh out 1–2 g. of zinc oxide in a porcelain crucible and ignite over the full flame of a Bunsen burner for 20 minutes or so in order to decompose any zinc carbonate that may be present; then allow to cool in a desiccator. Take the ignited zinc oxide and weigh out into 400 ml. beakers, three portions of 0.200 to 0.250 g. each, add to each beaker 14 ml. of 6 M hydrochloric acid,[16] and warm until the zinc oxide is dissolved. Add 10 g. of ammonium chloride dissolved in 50 ml. of water, and then dilute to 200 ml. Heat the solution to 70° and run in the potassium ferrocyanide solution, a few milliliters at a time with vigorous stirring, until the stoichiometric point is approached within a milliliter or so (this can be calculated in advance, since 1 ml. of 0.05 M potassium ferrocyanide solution ≡ 5 mg. of Zn ≡ 6 mg. of ZnO); then complete the titration by adding the ferrocyanide solution in small quantities of two or three drops at a time, and, after each addition, withdrawing a drop of the solution and mixing it thoroughly with the uranyl acetate indicator in one of the cavities of the spot-tile until the end point is reached, as described in § 266. Deduct the allowance previously determined for the end point as described in § 266 and calculate the value of the ferrocyanide solution in terms of zinc. The average deviation should not be more than 2 parts per 1,000.

It is very important to observe that, not only in the standardization of the ferrocyanide solution but also in the subsequent use of

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[15] Potassium ferrocyanide solutions are not particularly stable, and, therefore, they must be frequently restandardized.

[16] By using this amount of hydrochloric acid it will be unnecessary subsequently to adjust the acidity, as there will be an excess of free acid equivalent to about 6 ml. of 12 M HCl.

it in determining zinc in an unknown, the same correction for the end point must be made. Thus, suppose that in the standardization of the solution 40.00 ml. of it were required for 0.2456 g. of zinc oxide, and that 0.50 ml. of the solution was required to give an end point in the blank titration. The value of the solution would be $0.2456 \div (40.00 - 0.50) = 0.006218$ g. ZnO per milliliter. If now, the titration of the unknown required 20.00 ml. of standard solution, the corresponding amount of zinc oxide would be $(20.00 - 0.50) \times 0.006218 = 0.1212$ g. ZnO. If the analyst had failed to correct for the end point both in the standardization and in the determination of the unknown, he would report the amount of zinc oxide as 0.1228 g., which would mean an error of 13 parts per 1,000.

268. Exercise No. 23. Volumetric Determination of Zinc, Using an Outside Indicator. — Assuming that a sample requiring about 30 ml. of potassium ferrocyanide has been weighed out and dissolved, that the interfering metals have been separated as described in § 258 and that the zinc[17] is now in the form of sulfide, dissolve the precipitate of zinc sulfide from the filter paper into a 400 ml. beaker with about 35 ml. of 6 M hydrochloric acid and wash the filter paper thoroughly with hot water. Add 15 M ammonium hydroxide cautiously until a slight permanent precipitate (ZnS) is formed, add 6 ml. of 12 M hydrochloric acid and 5 g. of ammonium chloride,[18] dilute to 200 ml. heat to 70° and titrate with standard potassium ferrocyanide solution which is approximately 0.05 M, using 0.05 M uranyl acetate or uranyl nitrate as outside indicator. Allowance must be made for the end point, and all the details set forth in the preceding paragraphs must be observed.

269. Volumetric Determination of Zinc Using an Oxidation-reduction Indicator. — Either diphenylamine, $(C_6H_5)_2NH$, or diphenylbenzidine, $C_6H_5NH \cdot (C_6H_4)_2NH \cdot C_6H_5$, can be used as an oxidation-reduction indicator in the titration of Zn^{++} with $Fe(CN)_6^{\equiv}$. When either of the indicators is oxidized, it produces an intense

[17] If the zinc is in the form of a soluble salt to begin with and the only other substances present are sodium, potassium or ammonium salts, the prior precipitation of the zinc as zinc sulfide is unnecessary.

[18] This amount of ammonium chloride together with that formed in the previous neutralization of the hydrochloric acid will give a total of about 10 g., which is the amount that must be present in this determination. ,

violet color. This color can be removed by reduction. To a solution containing Zn^{++} and a small amount of indicator, sufficient $Fe(CN)_6^{\equiv}$ is added to give an oxidation potential high enough to oxidize the indicator to its colored form. The solution is then titrated with $K_4Fe(CN)_6$ to precipitate zinc as $K_2Zn_3[Fe(CN)_6]_2$. At the stoichiometric point, there will be a sudden increase in the concentration of $Fe(CN)_6^{\equiv}$ with an accompanying drop in oxidation potential below the value necessary to maintain the indicator in its colored form. The resulting disappearance of the violet color is the end point of the titration. A sharper end point can often be obtained by adding 1–2 ml. of $K_4Fe(CN)_6$ solution after the removal of the violet color and then back-titrating with a standard solution of Zn^{++} until the violet color is reestablished. Both diphenylamine and diphenylbenzidine form precipitates with the tungstate ion and hence this ion must be absent.

The same procedure can be used in standardizing the $K_4Fe(CN)_6$ solution as is used in the determination of zinc. A discussion of oxidation-reduction indicators is given in § 315.

270. Exercise No. 24. Volumetric Determination of Zinc, Using an Oxidation-reduction Indicator. — Weigh out and dissolve a sample requiring about 30 ml. of potassium ferrocyanide. Remove interfering metals as directed in § 258, precipitate the zinc as ZnS and wash as directed in § 259. Dissolve the precipitate in about 20 ml. of 6 M HCl and dilute the resulting solution to 100 ml. Then boil the solution to remove hydrogen sulfide and neutralize with NH_4OH solution. Add about 15 ml. of 5 M H_2SO_4 solution and then 10 g. of NH_4Cl. Cool the solution and add 2–4 drops of a 1% solution of diphenylamine or diphenylbenzidine indicator in 18 M H_2SO_4. Titrate the solution with standard $K_4Fe(CN)_6$ solution to the disappearance of the violet color.

An excess of 1–2 ml. of $K_4Fe(CN)_6$ solution may be added, and the solution back-titrated to the re-establishment of the violet color with 0.1 M zinc solution.

271. Zinc Ores.[19]— For convenience, zinc ores may be divided into two classes, namely, those which are soluble in mineral acids

[19] See "The Report of the Committee on Quantitative Methods," *Ind. Eng. Chem.*, **4,** 468 (1912), for a bibliography on zinc analyses.

and those which are only partially soluble in mineral acids. The most important ore of the soluble class is Sphalerite or Zinc Blende, ZnS, and (of less importance) Zincite, red oxide of zinc, ZnO, Smithsonite, $ZnCO_3$, Willemite, Zn_2SiO_4, and Calamine $H_2Zn_2SiO_5$ or $2\ ZnO \cdot SiO_2 \cdot H_2O$. These ores are likely to contain lead in considerable quantity, always iron and often copper, cadmium and sometimes antimony. The ores from Wisconsin, Missouri, Virginia, and the West all come under the class of soluble ores. The most important ore of the partially soluble class is Franklinite (Fe, Mn, Zn)$O \cdot$ (Fe, Mn)$_2O_3$, which occurs in large quantity at Franklin Furnace, New Jersey. Very often Franklinite will be accompanied by Willemite and Gahnite (Zinc Spinel) $ZnO \cdot Al_2O_3$, the latter ore being almost entirely insoluble. Franklinite contains large amounts of manganese but is practically free from members of the copper group.

272. Exercise No. 25. Determination of Zinc in Sphalerite (ZnS) or Other Soluble Zinc Ore. — Treat 0.5 g. of the finely ground ore in a covered casserole with 10 ml. of 12 M hydrochloric acid, heating gently until all violent action is over; add 5 ml. of 16 M nitric acid and 5 ml. of 18 M sulfuric acid and digest on the hot-plate until the ore is completely decomposed. Evaporate to copious fumes of sulfuric anhydride in order to expel all traces of hydrochloric and nitric acids, but take care not to go to dryness; allow the solution to cool, and, after estimating the amount of sulfuric acid which remains, add 50 ml. of water and enough more sulfuric acid to make the total concentration of the acid about 1.5 to 2 M. Introduce into the solution a piece of sheet aluminum about two inches square and bent up at its corners, and boil for about 10 minutes — this will usually serve for the complete reduction to the metallic state of any lead, copper, arsenic and antimony[20] that might be present, but any cadmium or bismuth will be only partially reduced. Filter the solution through a filter paper in which is placed a piece of metallic aluminum, and receive the filtrate in an Erlenmeyer flask. After washing the filter four or five times with small portions of hot water, cool the filtrate and washings to room temperature, add several drops of methyl orange

[20] Other metals completely reduced but very unlikely to be present are tin, cobalt, and nickel.

indicator, and neutralize with 15 M ammonium hydroxide; now add enough hydrochloric acid to make its concentration in the final volume equal to 0.3 M, heat the solution to 80°–90°, and pass in hydrogen sulfide to precipitate any cadmium[21] or bismuth and any traces of copper.   After the precipitate has settled, filter it off and wash with 0.3 M hydrochloric acid saturated with hydrogen sulfide.   The filtrate will now contain zinc, iron, manganese and perhaps calcium; it is boiled until free of hydrogen sulfide, and, if its volume is then greater than 125 ml., the boiling is continued until the volume is reduced to this amount; allow the solution to cool, add 2–3 drops methyl orange indicator, and 25 ml. of 1 M citric acid; then carefully neutralize with 3 M ammonium hydroxide, after which add 25 ml. of "formic mixture," and 25 ml. of 24 M formic acid; heat to boiling and pass in hydrogen sulfide to precipitate the zinc as zinc sulfide, observing all the details of § 259.   After the precipitate has settled, filter it off on filter paper and wash with 0.1 M formic acid saturated with hydrogen sulfide.   It is now ready for further treatment by any one of the methods described in §§ 263, 264 and 265.   Calculate to the "moisture-free basis" the amount of zinc found in the sample, running the necessary determination of moisture for this purpose on a separate 2 g. sample and conducting the drying to constant weight at 100°–105°.

273. Exercise No. 26.   Determination of Zinc in Franklinite[22] (Fe,Mn,Zn)O·Fe(Mn)$_2$O$_3$.—As already mentioned in § 271, Franklinite is not completely soluble in acids; it is, moreover, usually accompanied by Gahnite (Zinc Spinel) $ZnO \cdot Al_2O_3$ which is almost entirely insoluble.   It therefore becomes necessary to resort to fusion to decompose the insoluble residue which remains after the acid treatment.   If the residue contains considerable silica, it is best to use sodium carbonate as a flux, employing six parts by weight of the flux to one of residue; if the residue contains but little

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[21] It must be borne in mind that cadmium sulfide drags down zinc sulfide, so that if a considerable precipitate is obtained at this juncture it must be dissolved and reprecipitation effected.

[22] Stone, *Columbia School Mines Quarterly*, **8**, 150 (1887), reports the following analyses of samples of Franklinite:

	Fe$_2$O$_3$	Mn$_2$O$_3$	ZnO	MnO	
(Mine Hill, N. J.)	60.52	6.79	19.44	12.81	= 99.56%
	56.57	10.52	15.91	16.37	= 99.37%

silica, it is necessary to use borax glass (fused sodium borate) along with the sodium carbonate, employing 6 parts by weight of sodium carbonate and 3 parts of borax glass to one of residue.   It is to be remarked further that there is so much iron and manganese present in Franklinite that the chlorate and ammonia separations are not satisfactory for the subsequent removal of these elements.

Procedure. — Weigh out 1 g. of the finely ground ore and treat it in a covered casserole with 10 ml. of 12 M hydrochloric acid and 10 ml. of water, heating on the hot-plate.   Filter off the residue on filter paper and wash with small portions of hot water until free of chlorides; ignite in a platinum crucible and fuse with 6 parts by weight of sodium carbonate and 3 parts of borax glass to one of residue.   Dissolve the melt in hydrochloric acid and join with the main solution.   If either of the gravimetric methods involving $ZnSO_4$ or $ZnNH_4PO_4$ is to be used subsequently, then the combined solutions must be evaporated to dryness and baked at 105°–110° for 30 minutes or so to dehydrate the silica, which must be removed by filtration after getting the rest of the constituents back in solution (see § 215 for details of procedure).   If the volumetric method involving $Zn_3K_2[Fe(CN)_6]_2$ is to be used, the silica need not be removed.   In any event, the volume of the solution for further procedure should be about 125 ml.; if greater than this it must be reduced by boiling.   Allow the solution to cool, add 2–3 drops of methyl orange indicator and establish conditions for the hydrogen sulfide precipitation of the zinc as described in § 259.   After the precipitate of zinc sulfide has been obtained, the determination can be completed by any one of the methods described in §§ 263, 264 or 265.   Calculate to the "moisture-free basis" the amount of zinc found in the sample, running the necessary determination of moisture for this purpose on a separate 2 g. sample and conducting the drying to constant weight at 100°–105°.

274. Determination of Zinc in Alloys. — The chief alloys of zinc are brass, zinc base alloys and German silver.   Brass is an alloy of copper and zinc with small amounts of lead, tin and iron; the percentages will usually be within the following limits:

Copper	60–90%	Lead	1	Iron	max. 0.5
Zinc	18–40	Tin	1		

Zinc base alloys are alloys of zinc, copper and aluminum; or zinc, copper and tin. The composition varies considerably but the following percentages are typical:

Zinc	85%	Zinc	85%	Zinc	35%
Copper	10	Copper	5	Copper	5
Aluminum	5	Tin	10	Tin	60

German silver is an alloy of copper, zinc and nickel; iron is usually present in small quantity as an impurity. The percentages usually lie within the following limits:

Copper	50–60%	Nickel	15–25
Zinc	20–30	Iron	max. 0.5

In the analysis of zinc alloys which contain copper, the first thing to do after solution of the alloy is to remove the copper. As emphasized in § 258, the copper should not be removed by precipitation as the sulfide, because of the fact that copper sulfide drags down zinc sulfide; the copper should be removed by electrolysis from a 0.5–1.0 M solution of HNO_3 as described in § 416 or by electro-deposition with metallic aluminum from a fairly concentrated sulfuric acid solution (1.5–2.0 M H_2SO_4) which is free of nitrates or chlorides as described in the following paragraph.

275. Exercise No. 27. Determination of Zinc in German Silver. — Before being weighed, the sample should be carefully inspected and freed from any corrosion or foreign matter. Weigh out about 0.5 g. of sample and place in a 250 ml. beaker. Add 40 ml. of 8 M nitric acid and cover with a watch-glass. Heat cautiously if necessary. When solution is complete wash down the sides of the beaker with distilled water, cool, and add 10 ml. of 9 M sulfuric acid. Evaporate until dense fumes of sulfuric acid are given off. Cool, add 50 ml. of distilled water and one or two pieces of plate aluminum as described in § 258. Boil gently, keeping the flask well covered, until all action ceases. Filter, wash carefully, adding the washings to the original solution, and reject the precipitate. This treatment removes the major part of the copper. Cool the solution to room temperature, and neutralize with 6 M ammonium hydroxide, using methyl orange as indicator. Dilute to 100 ml. and add just enough hydrochloric acid to make its final concentration 0.3 M. Heat to 90°–95° and saturate the

solution with hydrogen sulfide. Allow the precipitate of CuS, which should be very slight at most, to settle; filter through filter paper and wash the precipitate five or six times with 0.3 M hydrochloric acid saturated with hydrogen sulfide; after being washed the precipitate can be rejected. Add the washings to the filtrate and boil the combined solution until the escaping steam no longer smells of hydrogen sulfide. If the volume of the solution is now greater than 125 ml., continue the boiling until the volume has been reduced to this value. Allow the solution to cool, add 2–3 drops of methyl orange indicator and 25 ml. of 1 M citric acid; then carefully neutralize with 3 M ammonium hydroxide, after which add 25 ml. of formic mixture and 25 ml. of 24 M formic acid; heat to boiling and pass in hydrogen sulfide to precipitate the zinc as zinc sulfide, observing all the details of § 259. After the precipitate has settled, filter it off on filter paper and wash with 0.1 M formic acid saturated with hydrogen sulfide. It is now ready for further treatment by any one of the methods described in §§ 263, 264 or 265. Calculate the per cent of zinc found in the sample.

276. Examples.

1. In determining the percentage of zinc in a sample of German silver, 0.4952 g. of sample was taken for analysis, and the zinc determined by precipitation as sulfide with subsequent conversion to the sulfate; the weight of zinc sulfate found was 0.2194 g. What was the percentage of zinc?   Ans.   17.94%.

2. In using a potassium ferrocyanide solution for zinc titrations the following results, inclusive of the amount of solution necessary to establish the end point, were obtained in the standardization:

Grams ZnO	ml. $K_4Fe(CN)_6$ used
0.2503	41.15
"	41.10
"	40.98

The blank for the end point required the following amounts of ferrocyanide solution: 0.60 ml., 0.50 ml., 0.55 ml. In titrating the zinc in a sample of ore, the following results, inclusive of the amount of solution necessary to establish the end point, were obtained:

Grams Sample	ml. $K_4Fe(CN)_6$ used
0.5007	20.38
0.5002	20.35

What was the percentage of Zn in the ore?   Ans.   19.66%.

CHAPTER XIV

ORGANIC PRECIPITANTS AND NON-AQUEOUS SOLVENTS

277. General Considerations. — Nearly all the gravimetric determinations and separations which we have thus far considered are those in which the precipitant has been inorganic in its nature and the solution has been essentially aqueous. In the case of some of the elements, however, it so happens that it is not possible to effect a satisfactory separation by such means, and therefore recourse has been had to the employment of organic precipitants in some instances and to the use of solvents other than water in other instances. Some of the more important organic precipitants which are employed at the present day are: diacetyl-dioxime (dimethylglyoxime), cupferron, nitron, and nitroso-β-naphthol; the more important solvents other than water are: ether saturated with hydrochloric acid, a mixture of absolute alcohol and ether in equal volumes, and amyl alcohol. The applications of these reagents follow herewith.

278. Diacetyl-dioxime (Dimethylglyoxime) as a Precipitant for Nickel. — Diacetyl-dioxime has the following structure,

$$CH_3 - C = NOH$$
$$| \qquad\qquad \text{Mol. wt. 116.1.}$$
$$CH_3 - C = NOH$$
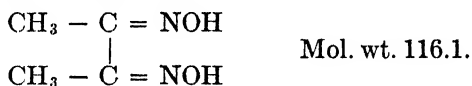
This reagent was first synthesized by L. Tschugaeff in 1905[1] and two years later was applied to the determination of nickel in steel by O. Brunck.[2] Diacetyl-dioxime reacts quantitatively with nickel ion to form the very insoluble precipitate

$$CH_3 - C = N - OH \qquad HO - N = C - CH_3$$
$$| \qquad\qquad\qquad\qquad\qquad | \qquad \text{Mol. wt. } \mathbf{288.8}$$
$$CH_3 - C = N - O - Ni - O - N = C - CH_3$$
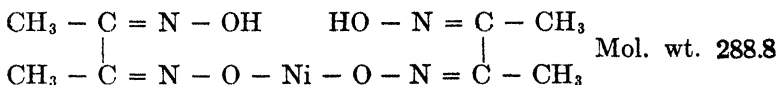
in which the content of nickel is 20.32%. This precipitate is one of the most satisfactory with which we have to deal since it can

[1] *Ber.*, **38**, 2520 (1905); *Z. anorg. Chem.*, **46**, 144 (1905).
[2] *Z. angew. Chem.*, **20**, 834 (1907).

be easily filtered and washed on a Gooch crucible and readily dried to constant weight at 110°–120°. When pure, it has a bright scarlet color with a characteristic golden luster.

With respect to the interference of other metals, it is to be noted that palladium and platinum give insoluble precipitates with diacetyl-dioxime, and cupric ion is co-precipitated with nickel diacetyl-dioxime from solutions having a pH more alkaline than 5, although cupric diacetyl-dioxime by itself is very soluble. Moreover, copper forms a complex with diacetyl-dioxime and when much copper is present the nickel may not be quantitatively precipitated unless a considerable excess of diacetyl-dioxime is added. Practically all the other metals with which nickel is found associated, such as cobalt, manganese, iron, chromium, aluminum, zinc, etc., do not interfere with the precipitation of nickel diacetyl-dioxime. It might be mentioned that before the advent of diacetyl-dioxime it was almost impossible to obtain a satisfactory determination of nickel in the presence of cobalt, whereas now it is a very simple matter.

Diacetyl-dioxime is insoluble in water but is slightly soluble in 95% alcohol, namely, to the extent of about 1 g. per 100 ml. of alcohol, in which form it is used as a reagent. If much more diacetyl-dioxime solution is used than is necessary to precipitate the nickel quantitatively, the excess of diacetyl-dioxime will itself precipitate out and contaminate the precipitate of nickel diacetyl-dioxime. Therefore, the diacetyl-dioxime should be added in slight excess only. This direction presupposes that the analyst knows beforehand the approximate nickel content of the solution from which the precipitation is being effected; if this knowledge is not at hand the analyst must make progressive additions of diacetyl-dioxime solution until assured that it is in slight excess, but not more than in slight excess. When copper is absent a smaller excess can be used than when copper is present.

279. Exercise No. 28. Determination of Nickel in a Nickel Ore. [3]— Weigh out the necessary quantity of ore to furnish not more than 0.100 g. of nickel, as the amount of nickel diacetyl-dioxime precipitate corresponding to this is the most that an

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[3] If a nickel ore is not at hand, a sample of German silver will answer equally well.

ordinary sized (20 ml.) Gooch crucible can accommodate.   Transfer to a 150 ml. beaker and add about 10 ml. of water; cover with a watch-glass and add 10 ml. of 12 M hydrochloric acid and 5 ml. of 16 M nitric acid.   Heat until decomposition of the ore is complete, adding a little bromine if necessary in the case of sulfide ores. After solution has been effected, dilute with hot water and filter into a 750 ml. beaker, washing the filter with hot water.   If there is any residue, fuse it with potassium pyro-sulfate in a quartz or porcelain crucible; dissolve the fusion by heating in 50 ml. of water containing about 5 ml of 9 M H_2SO_4; filter into the main solution.

To the combined filtrates, add, according to the amount of iron, aluminum, etc., present, about 50–100 ml. of 0.2 M citric acid.[4]   Now add 15 M ammonium hydroxide until the solution is faintly alkaline to litmus; if a precipitate forms, add more citric acid and again add ammonium hydroxide.   Now add 3 M hydrochloric acid until the solution is just acid to litmus paper; then add 3 ml. of 1 M hydrochloric acid.   It is very important to establish the acidity in accordance with the foregoing directions; if the acidity is much greater, the nickel diacetyl-dioxime will not precipitate; if the acidity is much less, copper will be co-precipitated with the nickel.   Dilute the solution to about 500 ml., add 10 g. of ammonium chloride, and heat to 60°–70°.   Add gradually and with constant stirring a 1% solution of diacetyl-dioxime in 95% alcohol (1 ml. ≡ 2.5 mg. nickel) until in slight excess, but no more than in slight excess.   Digest at 60°–70° for an hour; then add 10 ml. of 3 M ammonium hydroxide (this should make the solution slightly alkaline), and set aside to digest for 12 hours, allowing the solution to cool of its own accord.   Filter the precipitate through a weighed Gooch crucible which has been brought to constant weight in an electric oven at 110°–120°; wash with hot water until the washings are free of chloride.   During the filtration and washing keep the upper edge of the crucible dry for about $\frac{1}{4}$ inch down from the top as otherwise the precipitate will creep over the top and down the

[4] Tartaric acid or potassium sodium tartrate (Rochelle salt) may be used in place of citric acid for the purpose of forming complexes with the iron, aluminum, etc., to prevent their precipitation subsequently as hydroxides.   The use of tartaric acid or Rochelle salt, however, is not as advisable, owing to the likelihood of acid ammonium tartrate precipitating out in the preliminary adjustment of acidity prior to the addition of the diacetyl-dioxime.

outside of the crucible. Dry the crucible and its contents to constant weight at 110°–120° in the electric oven. The precipitate is $Ni(C_4H_7O_2N_2)_2$ and contains 20.32% nickel.

280. Exercise No. 29. Determination of Nickel in German Silver. — Weigh out about 0.5 g. of the alloy and place it in a 400 ml. electrolytic beaker and cover with a watch-glass. Add 20 ml. of 8 M nitric acid. When violent action ceases, boil until no more red fumes are given off. If tin is present it will precipitate as metastannic acid. If a precipitate forms, filter it off through filter paper and wash it thoroughly with 0.2 M nitric acid, testing the last few drops of each washing after the fourth with 0.2 M potassium ferrocyanide solution or 0.2 M ammonium sulfide solution until no precipitate or coloration is produced by either of these reagents. Dilute the solution and washings to 200 ml. and remove the copper electrolytically as described in §§ 435 and 416.

After the copper has been removed, transfer the solution to a 750 ml. beaker and add citric acid and then ammonium hydroxide as described in § 279. From this point continue the determination of nickel exactly as directed in § 279.

281. Benzildioxime, C_6H_5-C(NOH)-C(NOH)-C_6H_5. — The use of this reagent as a precipitant for nickel is described by Atack.[5] The nickel precipitate forms in less time than is often required when dimethylglyoxime is used. It is formed by adding an alcoholic solution of the reagent to an ammoniacal solution containing the nickel. This method is more suitable for quantities of nickel less than 0.025 g. than it is for larger amounts.

282. Cupferron. The Ammonium Salt of Nitrosophenyl Hydroxylamine. — Cupferron has the following structural formula,
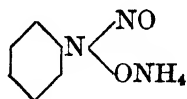
Mol. wt. 155.1.

Samples of this reagent on the market often contain a little zinc. It can readily be prepared according to the directions of Marvel & Kamm, *J. Am. Chem. Soc.* **41,** 276 (1919). This reagent precipitates copper, tin, iron, titanium, vanadium, zirconium and thorium from acid solutions and furnishes a method for separating these

[5] Atack, *Analyst.,* **38,** 316 (1913).

elements from cadmium, aluminum, chromium, manganese, cobalt, nickel, zinc, magnesium, calcium, barium and strontium.

It is particularly valuable in separating iron, zirconium, and titanium from manganese and aluminum, the details for this procedure being given by J. Brown, *J. Am. Chem. Soc.* **39,** 2358 (1917). Cupferron also precipitates silver, mercury, lead, bismuth, antimony (Sb^{+++}), molybdenum, uranium (U^{++++}), and cerium, but these separations have not as yet been fully worked out. A comprehensive review of the analytical uses of this reagent will be found in the article by Lundell and Knowles, *Ind. Eng. Chem.* **12,** 344 (1920), and Hillebrand and Lundell, "Applied Inorganic Analysis" p. 109, 1929. (See list of references § 11).

283. Nitron.   Diphenyl-endo-anilo-hydro-triazole. — Nitron has the following structural formula,
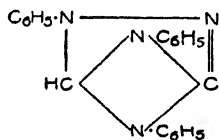
Mol. wt. 312.2.

This reagent, which is in reality a base, precipitates nitric acid as the fairly insoluble crystalline nitrate $C_{20}H_{16}N_4 \cdot HNO_3$.[6] In acid solutions the following anions also form more or less insoluble precipitates with nitron and must be absent in the determination of nitric acid: perchlorate, iodide, thiocyanate, chromate, chlorate, nitrite, ferrocyanide, ferricyanide, and bromide. The approxi-

Table 49

SOLUBILITIES OF SALTS OF NITRON

0.0099	g.	nitron	nitrate	equivalent to	0.0017	g.	HNO₃
.008	"	"	perchlorate	"	"	.002	"	HClO₄
.017	"	"	iodide	"	"	.005	"	HI
.04	"	"	thiocyanate	"	"	.007	"	HCNS
.06	"	"	chromate	"	"	.011	"	H₂Cr₂O₇
.12	"	"	chlorate	"	"	.022	"	HClO₃
.19	"	"	nitrite	"	"	.022	"	HNO₂
.61	"	"	bromide	"	"	.125	"	HBr

[6] M. Busch, *Ber.,* **38,** 861 (1905); A. Gutbier, *Z. angew. Chem.,* **18,** 494 (1905).

mate solubilities of the salts of the several acids with nitron, in 100 ml. of water, slightly acidulated with sulfuric acid, at 18°–22°, are given in Table 49.

284. Exercise No. 30.   Determination of Nitric Acid as Nitron Nitrate.[7] — Take enough of the sample to furnish about 0.100 g. of nitric acid and dissolve in 80–100 ml. of water with the addition of 10 drops of dilute sulfuric acid.   The solution is heated nearly to boiling and treated with 10–12 ml. of nitron acetate solution,[8] which is added all at one time.   The beaker containing the solution and precipitate is kept surrounded by ice water for about 2 hours.   The precipitate is then transferred to a Munroe crucible or to a Gooch crucible and drained as completely as possible from the pale yellow supernatant liquid.   It is washed with 10–12 ml. of ice water, added in small portions, and the precipitate drained well after each washing.   The precipitate is dried at 110° to constant weight.   It contains 16.53% of NO_3. On account of the appreciable solubility of the nitrate, it is to be expected that results should be a little low.   This is not the case, however, as Busch and Gutbier have proved.   It is probable that the precipitate occludes a little nitron acetate and in this way the error caused by the amount left in solution is compensated.

285. Alpha-Nitroso-Beta-Naphthol. — The structure of alpha-nitroso-beta-naphthol is as follows,
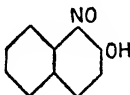
Mol. wt. 173.06.

This reagent precipitates the following elements from solutions which are slightly acid: copper, palladium, iron and cobalt; these metals may be quantitatively separated from antimony, aluminum, manganese, nickel, zinc, magnesium, calcium, barium and strontium.[9]   Probably the most important application of nitroso-

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[7] Quoting Treadwell-Hall, p. 401 of reference cited in § 11.

[8] The reagent is prepared by dissolving 10 g. of nitron in 100 ml. of 5% acetic acid.   The solution is usually straw-colored but darkens on exposure to the light.   It can be kept for a long time in a dark-colored bottle without undergoing any change.   .

[9] A résumé of these separations is given by Knorre, *Z. angew. Chem.*, **17**, 677 (1904).

β-naphthol is the determination of small amounts of cobalt in the presence of large amounts of nickel; for the separation of these two elements it is preferable to have them in the form of their sulfates or chlorides in a solution which is acidulated with hydrochloric acid; to this is added a hot solution of nitroso-β-naphthol in 50% acetic acid until all the cobalt is precipitated.[10]   The brick-red precipitate is then washed with cold 4 M hydrochloric acid, then with hot 4 M hydrochloric acid, and finally with water. For small amounts of cobalt, the precipitate may be ignited in air and weighed as Co_3O_4.

286. Phenyl Thiodantoic Acid, C_6H_5NC (NH_2) SCH_2COOH. — This reagent, having the structure,

$$\langle\hspace{-4pt}\rangle N=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle NH_2}{|}}{C}}-S-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \qquad \text{Mol. wt. 210.16,}$$
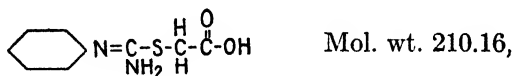
is a precipitant for cobalt.   The details of its use in separating cobalt from aluminum, chromium, vanadium, uranium, tungsten, molybdenum, arsenic, titanium, zinc, manganese, calcium, and magnesium is described by Willard and Hall.[11]   When iron is present, it will co-precipitate.   This co-precipitation can be diminished by the addition of citric acid.   Nickel if present will also co-precipitate.   Reagents which diminish the co-precipitation of nickel unfortunately have the effect of preventing complete precipitation of cobalt and, consequently, this method cannot be used as a means of separating cobalt from nickel.

[10] One of the authors (H. A. Fales) found that several samples of nitroso-β-naphthol obtained on the market precipitated nickel as well as cobalt.   He then prepared some nitroso-β-naphthol according to the original directions of C. E. Groves, *J. Chem. Soc.*, **45**, 294 (1884), and dissolved it in 50% acetic acid.   This preparation also precipitated nickel, but after standing several days at room temperature (18°–22°) a brown precipitate settled out; after this precipitate was filtered off, the solution no longer precipitated nickel.   It would seem from this experience that nitroso-β-naphthol is likely to be associated with some compound which arises in its synthesis and which precipitates nickel.   It is accordingly recommended that the analyst run a blank on every sample of nitroso-β-naphthol to determine whether it precipitates nickel or not.

[11] Willard and Hall, *J. Am. Chem. Soc.*, **22**, 19 (1922).

287. Benzoinoxime, $C_{14}H_{13}O_2N$. — This reagent may be used as a precipitant for copper in ammoniacal solution. The reaction taking place may be represented as follows:

or

$$C_{14}H_{13}O_2N + Cu^{++} \rightarrow (C_{14}H_{11}O_2N)Cu + 2H^+.$$
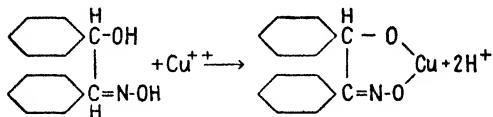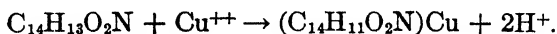
The application of this method to the determination of copper is described by Feigl.[12] Benzoinoxime is a precipitant for hexavalent molybdenum in acid solution. The details of a method of separating molybdenum by means of this precipitant are given by Knowles.[13] Kar[14] describes a method for the use of this reagent in the determination of copper in molybdenum alloy steels.

288. 8-Hydroxyquinoline HOC_9H_6N. — This reagent, having the structure,
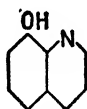
Mol. wt. 145.06,

forms slightly soluble precipitates with a number of metals. The completeness of precipitation, in many cases, depends, to a considerable extent, on the pH of the solution. Bismuth, copper, cadmium, nickel, cobalt, manganese, zinc, aluminum, ferric iron, and titanium are precipitated quantitatively from solutions containing acetic acid buffered with acetate ion. Magnesium and beryllium can be quantitatively precipitated from ammoniacal solution. Details for the quantitative separation of aluminum from beryllium are given by Kolthoff and Sandell.[15] Lundell and Knowles[16] describe the quantitative precipitation of aluminum

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[12] Feigl, *Ber.*, **56**, 2083 (1923); *Mikrochemie*, **1**, 76 (1923).

[13] Knowles, *Nat. Bur. of Standards, J. of Research*, **9**, 1 (1932).

[14] Kar, *Ind. Eng. Chem., Anal. Ed.*, **7**, 193 (1935).

[15] Kolthoff and Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928).

[16] Lundell and Knowles, *Nat. Bur. of Standards, J. of Research*, **3**, 91 (1929).

from solutions containing phosphorus, arsenic, boron, fluorine, tantalum, columbium, titanium, molybdenum, and uranium. Hahn and Vieweg [17] describe the details of the precipitation of magnesium from solutions containing the alkali metals. Berg [18] describes the quantitative precipitation of zinc from solutions containing magnesium and other metals. Zanko and Butenko [19] give a method for the precipitation of aluminum from solutions containing iron and titanium.

289. 5-7 Dibrom 8-Hydroxyquinoline. — Berg [20] reports that this substance precipitates titanium, copper, and iron quantitatively and that conditions can be arranged so that titanium can be quantitatively separated from copper, iron, mercury, chromium, and aluminum.

290. Phenylarsonic Acid, $C_6H_5AsO(OH)_2$. — Zirconium is precipitated by this reagent, and can be separated by this method from titanium and calcium. When thorium is present, its precipitation by means of phenylarsonic acid can be effected by buffering the solution with acetate ion. It is possible to determine zirconium and thorium from the same solution by means of this precipitant.

Stannic ion is quantitatively precipitated by means of phenylarsonic acid. The precipitate formed is converted to SnO_2 at 1,100° and weighed.

Rice, Fogg, and James [21] and Knapper, Craig, and Chandlee [22] discuss methods involving the use of phenylarsonic acid as a precipitant.

291. Tannin. — The precipitation of tantalum as tantalic acid can be effected by adding tannin to an oxalate solution containing the tantalum. To produce a similar reaction for niobium, a higher concentration and a lower acidity are required. It is possible, therefore, to effect a separation of tantalum from niobium by means of tannic acid.[23] Under proper conditions, tantalum,

[17] Hahn and Vieweg, *Z. anal. Chem.*, **71**, 122 (1927).

[18] Berg, *ibid.*, **71**, 171 (1927).

[19] Zanko and Butenko, *Zavodskaya Lab.*, **5**, 415 (1936).

[20] Berg, *Z. anorg. Chem.*, **204**, 215 (1932).

[21] Rice, Fogg, and James, *J. Am. Chem. Soc.*, **48**, 895 (1926).

[22] Knapper, Craig, and Chandlee, *ibid.*, **55**, 3945 (1933).

[23] Powell and Schoeller, *Analyst*, **50**, 485 (1925).

niobium, and titanium can be separated from uranium, zirconium, thorium, aluminum, and iron by the addition of tannin. Uranium in an oxalate solution containing a slight excess of ammonia is quantitatively precipitated by tannin.[24] Aluminum can be separated from beryllium,[25] and gallium from nickel, cobalt, manganese, zinc, cadmium, thorium, and beryllium by means of tannin.[26]

292. References to Quantitative Methods Using Organic Precipitants. — Table 50 contains by no means a complete list of references to organic precipitants, but gives references to some of the uses of organic precipitants in bringing about quantitative precipitation.

Table 50

ORGANIC PRECIPITANTS USED IN QUANTITATIVE ANALYSIS

Elements	Precipitants	References
Aluminum....	Tannin	Moser and Niessner, *Monatsh.*, **48**, 113 (1927).
		Moser and Singer, *Monatsh.*, **48**, 673 (1927).
	8-Hydroxyquinoline	Kolthoff and Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928).
		Zanko and Zavodskaya, *Chem. Abs.*, **30**, 5903, Sept. 10 (1936).
	Salicylic Acid	Young and Lay, *Contrib. Inst. Chem., Nat. Acad. Peiping*, **1**, 18 (1935).
Antimony....	Phenylthiodantoic Acid	Lassieur, *Compt. Rend.*, **176**, 1221 (1923).
Arsenic.......	8-Hydroxyquinoline	Schoorl, *Chem. Weekblad*, **56**, 325 (1919).
Barium.......	8-Hydroxyquinoline	Schoorl, *Chem. Weekblad*, **56**, 325 (1919).
Beryllium....	8-Hydroxyquinoline	Kolthoff and Sandell, *J. Am. Chem. Soc.*, **50**, 1900 (1928).
		Lundell and Knowles, *Nat. Bur. Standards, J. Research*, **3**, 91 (1929).

[24] Schoeller and Webb, *Analyst*, **58**, 143 (1933).

[25] Moser and Niessner, *Monatsh.*, **48**, 113 (1927); Moser and Singer, *ibid.*, **48**, 673 (1927).

[26] Moser and Brukl, *ibid.*, **50**, 667 (1928).

Table 50 — *Continued*

Elements	Precipitants	References
Bismuth......	8-Hydroxyquinoline	Berg, *Z. anal. Chem.*, **72**, 177 (1927).
	Pyrogallol	Feigl and Ordelt, *Z. anal. Chem.*, **65**, 448 (1925).
	Formaldehyde	Rupp and Hamann, *Z. anal. Chem.*, **87**, 32 (1931).
	Mercaptobenzothiozole	Spacu and Kuras, *Z. anal. Chem.*, **104**, 88 (1936).
Cadmium.....	Hexamethylenetetramine and allyl iodide	Everard, *Ann. chim. anal. chim. appl.*, **11**, 322 (1929).
	Ethylenediamine	Spacu and Suciu, *Z. anal. Chem.*, **77**, 340 (1929).
	Pyridine	Spacu and Dick, *Z. anal. Chem.*, **73**, 279 (1928).
	Alpha-Benzoinoxime	Knowles, *Nat. Bur. Standards, J. Research*, **9**, 1 (1932).
	Quinaldinic Acid	Ray and Bose, *Z. anal. Chem.*, **95**, 400 (1933)
Calcium......	Alizarin	Laidlav and Payne, *Biochem. J.*, **16**, 494 (1922).
	Malonic Acid, Potassium Cyanate	Macchia, *Chem.-Ztg.*, **52**, 281 (1928)
Chlorine......	Triphenyl tin chloride	Allen and Furman, *J. Am. Chem. Soc.*, **54**, 4625 (1932).
Cobalt.......	Dinitrosoresorcinol	Orndorff and Nichols, *J. Am. Chem. Soc.*, **45**, 1439 (1923).
	Alpha-Nitroso-beta-Naphthol	Jones, *Analyst*, **43**, 317 (1918).
		Eder, *Chem.-Ztg.*, **46**, 430 (1922). Cattelain, *J. Pharm. Chim.* [8], **2**, 525 (1925).
	Phenylthiodantoic Acid	Willard and Hall, *J. Am. Chem. Soc.*, **44**, 2219 (1922).
	Hydrorubeanic Acid	Ray and Ray, *J. Indian Chem. Soc.*, **3**, 118 (1926).
	Pyridine	Spacu and Dick, *Z. anal. Chem.*, **71**, 97 (1927).
Copper.......	Alpha-Benzoinoxime	Feigl, *Ber.*, **56**, 2083 (1923). Feigl, *Mikrochemie*, **1**, 76 (1923). Kar, *Ind. Eng. Chem. Anal. Ed.*, **7**, 193 (1935).
	Phenylthiodantoic Acid	Willard and Hall, *J. Am. Chem. Soc.*, **44**, 2219 (1922).

Table 50 — *Continued*

Elements	Precipitants	References
Copper (*continued*)	Pyridine	Spacu, *Z. Anal. Chem.*, **67**, 27 (1925). Spacu and Dick, *Z. Anal. Chem.*, **71**, 185 (1927)
	Isatin	Mencke, *Rec. Trav. Chim.*, **42**, 199 (1923).
	Nitrosophenylhydroxyl-amine ammonium salt (Cupferron)	Baudisch and King, *Ind. Eng. Chem.*, **3**, 629 (1911).
	Salicyl aldoxime	Ephraim, *Ber.*, **64**, 1210 (1931).
	Alpha-nitroso-beta-naphthol	Cattelain, *J. Pharm. Chim.*, **8** Serie 2, 525 (1925).
	Quinaldinic Acid	Ray and Bose, *Z. anal. Chem.*, **95**, 400 (1933). Ray and Gupta, *Mikromchemie*, **17**, 14 (1935).
	5–7 dibromhydroxy-quinoline	Hasse, *Z. anal. Chem.*, **78**, 113 (1929).
Gallium......	Tannin	Moser and Brukl, *Monatsh.*, **50**, 181(1928); *ibid.*, **51**, 325 (1929).
Iron.........	Nitrosophenylhydroxyl-amine ammonium salt (Cupferron)	Baudisch and King, *Ind. Eng. Chem.*, **3**, 629 (1911). Brown, *J. Am. Chem. Soc.*, **39**, 2358 (1917). Lundell and Knowles, *Ind. Eng. Chem.*, **12**, 344 (1920).
	Hexamethylenetetra-mine	Kollo, *Bul. Soc. Chim. Rom.*, **2**, 89 (1921).
	Alpha-nitroso-beta-naphthol	Knorre, *Z. angew. Chem.*, **17**, 677 (1904). Fontes and Thivolle, *Bul. Soc. Chim.*, **35**, 641 (1924). Cattelain, *J. Pharm. Chim.* [8], **2**, 525 (1925).
	5–7 dibromhydroxy-quinoline	Berg and Küstenmachu, *Z. anorg. Chem.*, **204**, 215 (1932).
Lead.........	Ammonium thiocya-nate-Pyridine	Spacu and Dick, *Z. anal. Chem.*, **72**, 289 (1927).
Magnesium...	Dimethylamine	Herz and Drucker, *Z. anorg. Chem.*, **26**, 347 (1901).
	8-Hydroxyquinoline	Berg, *Z. anal. Chem.*, **71**, 23 (1927). Hahn and Vieweg, *Z. anal. Chem.*, **71**, 122 (1927).

Table 50 — *Continued*

Elements	Precipitants	References
Manganese...	Pyridine	Spacu and Dick, *Z. anal. Chem.*, **74,** 188 (1928).
Mercury.....	Propylenediamine	Spacu and Spacu, *Z. anal. Chem.*, **89,** 188 (1932).
	Pyridine-Ammonium dichromate	Spacu and Dick, *Z. anal. Chem.*, **76,** 273 (1929).
Molybdenum	Nitrosophenylhydroxyl-amine ammonium salt (Cupferron)	Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **5,** 305 (1933).
	Alpha-Benzoinoxime	Knowles, *Nat. Bur. Standards, J. of Research*, **9,** 1 (1932).
		Kar, *Ind. Eng. Chem. Anal. Ed.*, **7,** 193 (1935).
Nickel.......	Alpha-Benzil Dioxime	Atack, *Analyst*, **38,** 316 (1913).
	Dicyandiamidine Sulfate	Grossman and Schück, *Chem.-Ztg.*, **31,** 335, 911 (1907).
	Diacetyl-dioxime	Brunck, *Z. angew. Chem.*, **20,** 834 (1907).
		Weeldenburg, *Chem. Weekblad*, **21,** 358 (1924).
	Hydrorubeanic Acid (dithiooxamid)	Ray and Ray, *J. Indian Chem. Soc.*, **3,** 118 (1926).
	Methylbenzoyl glyoxime	Hanus, Jélek and Lucas, *Chem. News*, **131,** 401 (1925).
		Holzer, *Z.anal.Chem.*,**95,** 392(1933).
	Alpha-Furildioxime	Soule, *J. Am. Chem. Soc.*, **45,** 981 (1925).
	Pyridine	Spacu and Dick, *Z. anal. Chem.*, **71,** 442 (1927).
Niobium.....	Tannin	Powell and Schoeller, *Analyst*, **50,** 485 (1925).
		Schoeller and Webb, *Analyst*, **58,** 143 (1933).
Nitrate......	Diphenyl-endo-anilo-hydrotriazole	Busch, *Ber.*, **38,** 861 (1905).
		Guthier, *Z. angew. Chem.*, **18,** 494 (1905).
Palladium....	Diacetyldioxime	Graulich, *Chem. Abs.*, **24,** 1599 (1930).
	6-Nitroquinoline	Ogburn and Riesmeyer, *J. Am. Chem. Soc.*, 50, 3018 (1928).
	Alpha-Nitroso-beta-Naphthol	Schmidt, *Z. anorg. Chem.*, **80,** 335 (1913).
		Cattelain, *J. Pharm. Chim.* [8], **2,** 525 (1925).

Table 50 — *Continued*

Elements	Precipitants	References
Platinum.....	Diacetyldioxime	Graulich, *Chem. Abs.*, **24,** 1599 (1930).
	Formic Acid	Treadwell-Hall, "Analytical Chemistry," Vol. II, 8th ed., p. 260, John Wiley & Sons, Inc., New York, 1935.
Potassium....	Sodium-5-Nitro-6-Chlorotoluene-3-Sulfonate	Davies and Davies, *J. Chem. Soc.*, **123,** 2976 (1923).
	Dipicrylamine	Winkel and Maas, *J. angew. Chem.*, **49,** 827 (1936).
	d-l-Tartaric Acid	Szebelledy and Jonas, *Z. anal. Chem.*, **107,** 114 (1936).
Selenium	Hydroxylamine hydrochloride	Lehner and Kao, *J. Am. Chem. Soc.*, **47,** 2456 (1925).
Silver........	p-Dimethylaminobenzal-Rhodanine	Kolthoff, *J. Am. Chem. Soc.*, **52,** 2222 (1930).
	Chromotropic Acid	Gutzeit, *Helv. Chim. Acta.*, **12,** 714 (1929).
	Methylamine	Martini, *Mikrochemie,* **7,** 233 (1929).
Tantalum....	Tannin	Powell and Schoeller, *Analyst*, **50,** ·485 (1925).
		Schoeller and Webb, *Analyst*, **58,** 143 (1933).
Tellurium....	Hydrazine hydrochloride	Lehner and Kao, *J. Am. Chem. Soc.*, **47,** 2456 (1925).
	Hydroquinone	Putnam, Roberts and Selchow, *Am. J. Sci.*, **15,** 253 (1928).
Thorium.....	Phenylarsonic Acid	Rice, Fogg, and James, *J. Am. Chem. Soc.*, **48,** 895 (1926).
Tin..........	Nitrosophenyl hydroxylamine ammonium salt (Cupferron)	Kling and Lassieur, *Compt. Rend.*, **170,** 1112 (1920).
		Furman, *Ind. Eng. Chem.*, **15,** 1071 (1923).
	Phenylarsonic Acid	Knapper, Craig and Chandlee, *J. Am. Chem. Soc.*, **55,** 3945 (1933).
Titanium.....	Nitrosophenyl hydroxylamine ammonium salt (Cupferron)	Brown, *J. Am. Chem. Soc.*, **39,** 2358 (1917).
		Lundell and Knowles, *Ind. Eng. Chem.*, **12,** 344 (1920).
		Von Bergkampf, *Z. anal. Chem.*, **83,** 345 (1931).
		Cunningham, *Ind. Eng. Chem., Anal. Ed.*, **5,** 305 (1933).

Table 50 — *Continued*

Elements	Precipitants	References
Titanium (*continued*)	8-Hydroxyquinoline	Berg and Teitelbaum, *Z. anal. Chem.*, **81**, 1 (1930).
	5-7-Dibrom-8-hydroxy-quinoline	Berg and Kustenmacher, *Z. anorg. Chem.*, **204**, 215 (1932).
	Tannin	Powell and Schoeller, *Analyst*, **55**, 605 (1930).
		Schoeller and Webb, *Analyst*, **58**, 143 (1933).
	Alpha-Benzoinoxime	Knowles, *Nat. Bur. Standards, J. Research*, **9**, 1 (1932).
Tungsten.....	Benzidine	Knorre, *Ber.*, **38**, 783 (1905).
	Cinchonine	Hillebrand and Lundell, "Applied Inorganic Analysis," p. 553, John Wiley and Sons, Inc., New York, 1929.
	Phenylhydrazine hydro-chloride	Dotreppe, *Bul. soc. chim. Belg.*, **38**, 385 (1929).
Uranium.....	Tannin	Schoeller and Webb, *Analyst*, **58**, 143 (1933).
	Quinaldinic Acid	Ray and Bose, *Z. anal. Chem.*, **45**, 400 (1934).
Vanadium....	8-Hydroxyquinoline	Sandell, *Ind. Eng. Chem., Anal. Ed.*, **8**, 336 (1936).
Zinc.........	8-Hydroxyquinoline	Berg, *Z. anal. Chem.*, **71**, 171 (1927).
	Pyridine	Spacu and Dick, *Z. anal. Chem.*, **73**, 356 (1928).
	Quinaldinic Acid	Ray and Bose, *Z. anal. Chem.*, **95**, 400 (1934).
		Ray and Bose, *Mikrochemie*, **17**, 11 (1935).
Zirconium....	Phenylarsonic Acid	Rice, Fogg, and James, *J. Am. Chem. Soc.*, **48**, 895 (1926).
	n-Propylarsonic Acid	Arnold and Chandlee, *J. Am. Chem. Soc.*, **57**, 8 (1935).
	Tannin	Schoeller and Waterhouse, *Analyst*, **52**, 515 (1928).
		Schoeller and Powell, *Analyst*, **57**, 550 (1932).
	Nitrosophenyl hydrox-ylamine ammonium salt (Cupferron)	Brown, *J. Am. Chem. Soc.*, **39**, 2358 (1917).

293. Non-aqueous Solvents. — Substances whose solubilities in water do not differ sufficiently to permit of quantitative separation in water solution in some cases differ widely in their solubilities in some non-aqueous solvent. Extraction of a mixture of the substances in the solid form or extraction of a water solution of the substances by means of a suitable non-aqueous solvent may sometimes be used to bring about a quantitative separation of the substances.

The separation of sodium from potassium is effected by using 80% alcohol to remove the sodium chloroplatinate, $Na_2PtCl_6 \cdot 6H_2O$, from a mixture of sodium chloroplatinate and potassium chloroplatinate, K_2PtCl_6. The details for this method are given in § 469. Other illustrations of separations making use of non-aqueous solvents are given in succeeding paragraphs.

294. Ether Saturated with Hydrochloric Acid. — As first shown by W. Skey,[27] if a hydrochloric acid solution of ferric chloride is shaken up with ether and the mixture allowed to separate into two layers; the ether layer will contain more or less of the ferric chloride, depending upon the relative volumes of the ether and the water layers and upon the concentration of the hydrochloric acid in the ferric chloride solution. Rothe,[28] however, was the first to apply this principle to the technical analysis of iron compounds, and the method is usually referred to as "Rothe's Ether Method." The most favorable concentration of hydrochloric acid is 6.0 M; if much above or below this molarity, then the percentage of ferric chloride which passes into the ether layer is considerably diminished, as shown by the investigation of Speller.[29] This author found that when 0.8 g. of iron in the form of ferric chloride was dissolved in 100 ml. of hydrochloric acid of the molarity given, shaken with twice its volume of ether, and allowed to stand 30 minutes at 17°–18°, the ether layer contained the percentage of iron given in Figure 55. These results show that two or three extractions with ether are sufficient to remove practically all the iron from a 6 M hydrochloric acid solution.

[27] *Chem. News*, **36**, 48 (1880).

[28] J. W. Rothe, *Mitt. kgl. tech. Versuchsanstalt, Berlin*, **10**, 132 (1892); *Chem. News*, **66**, 182 (1892); *Stahl u. Eisen*, **12**, 1052 (1892).

[29] F. N. Speller, *Chem. News*, **83**, 124 (1901).

The ether used should be first saturated with hydrochloric acid by shaking it with some 12 M HCl, for, if ordinary ether is used, the amount of hydrochloric acid in the aqueous layer will be decreased by each extraction. The chlorides of thallium,[30]

Molarity of Acid	% Iron in Ether Layer
2.41	0.4%
3.04	1.6
3.50	13.0
4.07	52.5
4.92	90.0
5.40	96.7
6.19	98.1
6.34	98.1
6.72	98.0
7.00	97.6
7.50	92.8
9.36	26.0
9.85	7.16
10.3	2.5
12.5	1.0
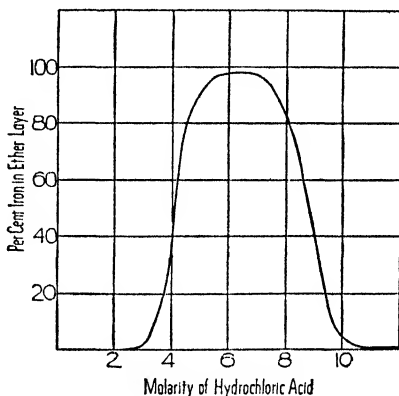
Fig. 55

Extraction of Iron from Hydrochloric Acid Solution with Ether

gold,[31] tungsten and molybdenum,[32] if present, are more or less completely removed with the ferric iron in the ether layer; the same thing is true of the chlorides of stannous tin and mercuric mercury.[33]

Extraction of Phosphorus. — If phosphorus is present as ortho-phosphate, a considerable portion of it, depending upon the

[30] A. A. Noyes, W. C. Bray, E. B. Spear, *J. Am. Chem. Soc.*, **30**, 22 (1908).

[31] R. Willstätter, *Ber.*, **36**, 1830 (1903), separates gold chloride from platinum chloride in aqueous solutions by extracting with ether.

[32] Molybdenum appears to be but imperfectly separated in the absence of ferric chloride. W. Skey, *Chem. News*, **36**, 48 (1880); A. A. Blair, *J. Am. Chem. Soc.*, **30**, 1229 (1908); R. de Jong, *Z. anal. Chem.*, **41**, 596 (1902).

[33] The chlorides of sodium, potassium, calcium, nickel, zinc and cadmium, and the thiocyanates of copper, nickel and zinc are soluble in anhydrous but not in aqueous ether: W. Skey, *Chem. News*, **36**, 48 (1880). Stannous chloride is soluble in ether: M. de Jong, *Z. anal. Chem.* **41**, 596 (1902).

amounts of iron and phosphorus present, goes along with the iron into the ether layer as shown by Wysor,[34] whose results are given in Table 51.

Table 51

EXTRACTION OF ORTHO-PHOSPHATE BY ETHER SATURATED WITH HYDRO-CHLORIC ACID IN THE PRESENCE OF VARYING AMOUNTS OF IRON

Weight of Phosphorus Taken (as P_2O_5)	Weight Phosphorus (as P_2O_5) Accompanying Ferric Chloride from		
	1 g. Fe	2 g. Fe	3 g. Fe
0.0023 g.	0.0005	.....	..... g.
0.0046 "	0.0009	0.0015	0.0017 "
0.0092 "	0.0016	0.0029	0.0032 "
0.0182 "	0.0031	0.0055	0.0064 "
0.0366 "	0.0060	0.0108	0.0130 "

Rothe's Ether Method finds special application in the analysis of iron ores and iron and steel products when it is desired to determine the amounts of other elements that may be present with the iron, but present in small amounts only, in particular, copper, aluminum, chromium, titanium, vanadium, manganese, nickel, cobalt, calcium, magnesium and sulfur.   The iron will go into the ether layer, the other elements into the aqueous layer as already mentioned, and molybdenum and phosphorus (ortho-phosphate) will divide more or less between the two layers.

295. Exercise No. 31.   Rothe's Ether Method Applied to Iron Ore. — Dissolve 5–10 g. of the ore in hydrochloric acid.   Evaporate the resulting solution to dryness on the water-bath and maintain at the temperature of the water-bath for 20 minutes or so to dehydrate silica.   Add 50 ml. of 6 M hydrochloric acid, digest for several minutes at 50°–60°, dilute with 50 ml. of water and filter off the residue, consisting of insoluble matter and dehydrated silica.   Treat the residue in a platinum crucible with several milliliters of hydrofluoric acid and 2–3 drops of sulfuric acid, evaporating to dryness but not igniting.   Dissolve

[34] R. J. Wysor, *Ind. Eng. Chem.*, **2**, 45 (1910).

the residue in hydrochloric acid, filter off any insoluble matter, and add the filtrate to the main solution.   The insoluble matter, which will be very small, is free of iron and therefore need not be included in the ether separation.   Fuse it with a little sodium carbonate or potassium pyrosulfate, dissolve the fused mass in hydrochloric acid, and subsequently add the resulting solution to the aqueous layers from which the iron has been extracted. Evaporate the main solution, plus the filtrate from the hydro-fluoric acid treatment to a syrupy consistency on the water-bath, add 10–15 ml. of 6 M hydrochloric acid, and transfer the whole contents to a short stem separatory funnel of about 150 ml. capacity.   If any of the ferric chloride solution remains behind, rinse it into the separatory funnel with a little 6 M hydrochloric acid, but keeping the amount of acid used as small as possible because the total volume of ferric chloride solution in the separatory funnel should not exceed 50 ml.

Cool the separatory funnel and its contents by holding under the tap water, and add cautiously 50 ml. of ether previously saturated with hydrochloric acid.   Mix the two layers by gently shaking, keeping the funnel under the tap water, as much heat is generated, and if the heat is not removed the consequent rise in temperature will cause the ether to reduce some of the ferric iron to ferrous.   This should be avoided since the ferrous chloride will go into the aqueous layer.   Even with the most careful manipulation in shaking, there will always be a considerable increase in the vapor pressure of the ether, and the caution must be carefully observed to open the stop-cock of the separatory funnel frequently during the shaking in order to relieve the pressure. After the contents of the funnel have been thoroughly shaken and mixed, set the funnel aside for 30 minutes or so until the two layers have completely separated.   Then run the lower, aqueous layer into a second separatory funnel.   Rinse the stopper and stem of the first funnel carefully with 6 M hydrochloric acid and add the rinsings to the second funnel.   Add 50 ml. of 6 M hydrochloric acid to the first funnel, and repeat the extraction. Then combine the lower aqueous layer with the one already in the second separatory funnel.   Now add 50 ml. of ether (previously saturated with hydrochloric acid) to the second funnel.   Repeat

the shaking, etc., in order to extract more of the ferric chloride from the combined aqueous layers. After the ether layer has been allowed to separate completely from the aqueous layer, draw off the latter into a beaker and free it from dissolved ether by evaporating on a steam bath (care must be taken that no flames are near). The aqueous layer will contain about 5% of the iron originally present in the sample. This will be mostly in the ferric form, although a little of it may be reduced to the ferrous form through the reducing action of the ether. If it is desired to remove more of the iron, another extraction with ether can be made. The aqueous layer will also contain all of the following elements if they were originally present in the sample: copper, aluminum, chromium, titanium, vanadium, manganese, nickel, cobalt, calcium, and magnesium; also about 70% of the phosphorus. If molybdenum or tungsten were present, they will be found mostly, if not entirely, with the ether layer.
ι   After the aqueous layer has been freed of dissolved ether, add a little nitric acid and boil the solution to oxidize any ferrous iron to ferric. The solution is now ready for any separations that may be desired.

296. Exercise No. 32. Rothe's Ether Method Applied to Steel. — Dissolve 2–3 g. of the steel in nitric acid with the aid of hydrochloric acid if necessary. Evaporate the resulting solution to dryness on the water-bath for 20 minutes or so to dehydrate any silica. Add 30 ml. of 6 M hydrochloric acid, digest for several minutes at 50°–60°, dilute with 30 ml. of water and filter off any silica. Evaporate the filtrate on the water-bath until it reaches a syrupy consistency. Add 10–15 ml. of 6 M hydrochloric acid and transfer the solution to a separatory funnel of about 150 ml. capacity, using a little more 6 M hydrochloric acid for rinsing purposes; the total volume of the ferric chloride solution in the separatory funnel should not exceed 50 ml. Cool the separatory funnel under the tap water and proceed as directed in the method for iron ore.

297. Extraction with a Mixture of Absolute Alcohol and Ether in Equal Volumes. — The use of this mixture allows the separation of calcium from strontium (barium); the nitrate of calcium is soluble in the mixture while the nitrate of strontium is not. The

method is used in rock analysis [35] as follows: The weighed oxide (CaO + SrO) from the ammonium oxalate precipitation of the calcium is transferred to a small flask of 20 ml. capacity, dissolved in nitric acid, and evaporated to dryness at 150°–160°. The thoroughly dried nitrates are treated with as little (seldom over 2 ml.) of a mixture in equal parts of absolute alcohol and ether as may be needed to dissolve the calcium salt, solution being hastened by occasional gentle agitation. After standing overnight in the corked flask the insoluble matter is collected on the smallest possible filter and washed with more of the above mixture of alcohol and ether. After drying, a few milliliters of hot water are passed through the filter, on which may remain a few tenths of a milligram of residue, which does not usually contain any lime or other alkaline earth and whose weight is therefore to be deducted from that of the lime, unless it can be shown that it is derived from the glass of the little flask in which the nitrates of calcium and strontium were evaporated. To the solution of strontium nitrate in a small beaker a few drops of sulfuric acid and then its volume of alcohol are added, whereby the strontium is precipitated as sulfate, in which form, after 12 hours, it is weighed and then tested spectroscopically as to freedom from calcium and barium.

298. Amyl Alcohol. Separation of Lithium from Sodium and Potassium. — The use of this solvent forms the basis of Gooch's [36] method for the separation of lithium from sodium and potassium. Anhydrous lithium chloride is soluble in boiling amyl alcohol while the chlorides of the other two elements are but very sparingly soluble. Gooch thus describes his method for separating lithium :[37]

"To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first, to avoid danger of bumping, until the water disappears from solution and the point of ebullition rises and becomes constant for some minutes at a temperature which is approximately that at which the alcohol

[35] Hillebrand, pp. 142–144 of reference given in § 11.

[36] *Proc. Am. Acad. Arts Sci.* p. 177 (1886); *U. S. Geol. Survey Bull.* No. 42, pp. 85–86 (1887); *Chem. News*, **55**, 18, 29, 40, 56, 78 (1887); *J. Am. Chem. Soc.*, **9**, 33 (1887). Consult, also, W. W. Skinner and W. D. Collins, *Bull. Bur. Chemistry*, No. 153 (1912).

[37] Hillebrand, p. 212 of reference given in § 11.

boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation, the liquid is cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small, it will now be found in solution and the chlorides of sodium and potassium will be in the residue, excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds 10 or 20 mg., it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol, previously dehydrated by boiling, is to be used, and the filtrates are to be measured apart from the washings. In filtering, it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of the insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0.00041 g. for every 10 ml. of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is entirely sodium chloride; 0.00051 g. for every 10 ml. if potassium chloride constitutes the residue, and if both sodium and potassium chlorides are present, 0.00092 g.; but . . . the entire correction may, in any case, be kept within very narrow limits if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulfuric acid, the excess of the latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0.0005 g. is to be made if sodium chloride constitutes the precipitate; 0.00059 g. if potassium chloride alone is present in the residue, and 0.00109 g. if both these chlorides are present, for every 10 ml. of filtrate, exclusive of washings.

"Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature — the development

of the fumes of amyl alcohol — is one which is insignificant when good ventilation is available.

"The process has been used for some months frequently and successfully, by others as well as myself, for the estimation of lithium in waters and minerals."

299. Examples.

1. The nickel in a 1.0426 g. sample of nickel ore, containing 3.13% moisture, was precipitated with diacetyl-dioxime. The weight of precipitate was 0.2199 g. Calculate the per cent of nickel in the sample on the dry basis.

2. In the analysis of an alloy of Ni, Cr, Mn and Fe for Nickel, 0.1340 g. sample yielded 0.5111 g. nickel dimethylglyoxime. What was the percentage of nickel?   Ans. 77.48%.

3. In determining nickel in a nickel ore by means of diacetyl-dioxime,
   (a) Why is citric acid added?
   (b) Why is the solution made alkaline with NH_4OH and then acid with HCl prior to the precipitation of the nickel?

4. In "Rothe's Ether Method" would the completeness of extraction of iron be affected by the failure of the analyst to cool the separatory funnel while adding the ether? Explain.

5. In their studies on the Analytical Chemistry of Tungsten and Molybdenum, Yagoda and Fales, *J. Am. Chem. Soc.* **60,** 640 (1938), employed α-benzoin oxime as a precipitant for tungsten, igniting the tungsten-benzoin oxime to tungstic oxide, with the following results:

Na_2WO_4	WO_3, g. found
0.0500	0.0348
0.0250	0.0178
0.0250	0.0170
0.0100	0.0065
0.0100	0.0067

Tungstic oxide redissolved after ignition and weighed as Tl_2WO_4. Obtain the calculated amounts of WO_3 and compare them with those found.

6. In the analysis of an alloy of Ni, Cr, Mn and Fe, the following results had been obtained for the first three constituents: Ni 62.68%; Cr 11.12%; Mn 3.72%. 0.4514 g. of the alloy were then used for the determination of the iron which was precipitated by means of cupferron; the precipitate was ignited to the oxide, yielding 0.1466 g. Fe_2O_3. What was the percentage of iron found? What was the total percentage of all the constituents?   Ans. 22.57% Fe, 100.09% Total.

CHAPTER XV

OXIDATION-REDUCTION THEORY[1]

300. General Considerations. — Oxidation-reduction reactions are based upon the fact that metals, non-metals, and their ions can be made to undergo a change in the amount of electric charge associated with them, and that in this change there is a simple relationship between the quantity of electricity gained or lost and the weight of the substance which is affected. This relationship is embodied in Faraday's Law, which may be reworded to read: *A change of charge of one corresponds to the gain or loss of 96,500 coulombs [2] of electricity per formula weight of the substance involved.* Since in every oxidation-reduction reaction the charge which is lost by one reacting substance must of necessity be gained by the other, it follows that there is always a transfer of electricity, and, consequently, the two important factors that we have to consider are:

1. The change of charge which takes place.

2. The electromotive force (e.m.f.) associated with the transfer of charge.

301. *The Change of Charge Which Takes Place.* — By way of introduction to this first factor, let us take the example of the reduction of ferric chloride by means of stannous chloride. The addition of stannous ions to a solution of ferric ions may result in the following reaction,

$$Sn^{++} + 2\,Fe^{+++} \rightarrow Sn^{++++} + 2\,Fe^{++}.$$
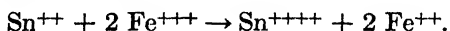
[1] Stieglitz, Chapters XIV and XV of reference given in § 11.

[2] The value of 96,500 coulombs is the one most recently accepted for the value of the Faraday. See H. S. Taylor, "A Treatise on Physical Chemistry," Vol. I, 2nd ed., p. 631, D. Van Nostrand Co., New York, 1936, citing: Washburn and Bates, *J. Am. Chem. Soc.*, **34**, 1341 (1912); Bates, *ibid.*, **34**, 1515 (1912); Bates and Vinal, *ibid.*, **36**, 916 (1914); Vinal and Bovard, *ibid.*, **38**, 496 (1916). The previously accepted value of the Faraday was 96,540 coulombs.

The change taking place here is essentially a transfer of two electrons from one stannous ion to two ferric ions with the consequent formation of one stannic ion and two ferrous ions. This change may be expressed by means of the following partial equations,

$$Sn^{++} \rightarrow Sn^{++++} + 2\ e,$$
$$2\ e + 2\ Fe^{+++} \rightarrow 2\ Fe^{++}.$$
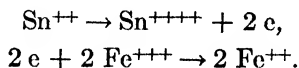
Reactions of this sort, involving a transfer of electrons are known as *oxidation-reduction reactions*. The loss of electrons is known as *oxidation*. Thus the stannous ion is oxidized to stannic ion. The gain of electrons is known as *reduction*. In the above illustration, the ferric ions are reduced to ferrous ions. That there is an actual transfer of electrons from stannous to ferric ions can be shown by the following experiment:

Tenth molar solutions of ferric chloride and stannous chloride, acidulated with hydrochloric acid to increase the conductivity, are placed in separate beakers and connected by a "salt bridge," containing a saturated solution of sodium chloride, as
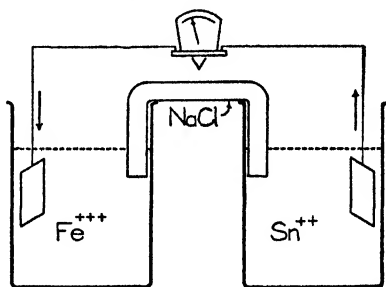
Fig. 56

Ferric Chloride-Stannous Chloride Cell

represented in Figure 56. Platinum electrodes connected to a delicate voltmeter are introduced into the solutions as shown. Upon completion of the circuit, the deflection of the voltmeter indicates the passage of electrons through the external circuit from the stannous chloride solution to the ferric chloride solution. When the current has flowed for a short time, it is possible to show that ferrous ions have been formed in the solution containing the ferric chloride and stannic ions have been formed in the solution containing the stannous chloride. The chloride ion undergoes no change since it is in the same state of oxidation after the reaction as before it.

Since each stannous ion loses two electrons to two ferric ions, it follows that the oxidation of 118.7 g. of stannous ion involves

the loss of $2 \times 96,500$ coulombs of negative electricity and the reduction of 2×55.84 g. of ferric ion.

302. Electromotive Force Associated with the Change of Charge. — In the experiment just considered, the fact that electrons flow from the electrode in the stannous chloride solution to that in the ferric chloride solution indicates that a difference of potential exists between the two electrodes. This difference of potential is an essential requisite for the progress of an oxidation-reduction reaction. Due to the great importance of this electromotive force, it is advisable to consider at this point not only the factors which determine its value, but also its relationship to the change in charge with which it is associated.

303. Oxidant-Reductant Systems. — We have seen that when ferric ion acquires one electron it becomes ferrous ion and that when ferrous ion loses one electron it becomes ferric ion. These two tendencies may be represented as follows,

$$Fe^{+++} + 1 e \rightleftarrows Fe^{++}.$$
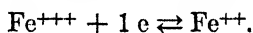
The two ions involved may be considered to be members of the ferric-ferrous system. The member of the system which tends to combine with electrons is known as the *oxidant*. Thus, in the ferric-ferrous system the ferric ion is the oxidant. The member of a system which tends to liberate electrons is known as the *reductant*. In the system being considered, the ferrous ion is the reductant. Likewise, we can represent the stannic-stannous system as follows,

$$Sn^{++++} + 2 e \rightleftarrows Sn^{++},$$
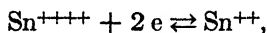
in which the stannic ion is the oxidant and the stannous ion is the reductant. For the ceric-cerous system we have,

$$Ce^{++++} + 1 e \rightleftarrows Ce^{+++},$$
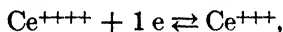
and for the permanganate-manganous system,

$$5 e + 8 H^+ + MnO_4^- \rightleftarrows Mn^{++} + 4 H_2O.$$
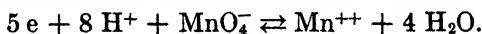
The hydrogen ion-hydrogen system may be represented by the following,

$$2 H^+ + 2 e \rightleftarrows H_2.$$
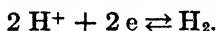
If into a solution containing this system we insert a platinum electrode, hydrogen ions in the solution will tend to remove

electrons from the electrode, and thereby give it a positive charge. Uncharged hydrogen in the solution will tend to lose electrons to the electrode and thereby give it a negative charge. These two opposing tendencies will reach equilibrium ·sooner in the presence of a catalyst. A deposit of finely divided platinum on the surface of the electrode will serve this purpose. At equilibrium, the potential of the electrode may be considered a measure of the tendency of the system, under a given set of conditions, to acquire electrons. The equilibrium potential of a system is often referred to as its oxidation potential. .In the case of the hydrogen ion-hydrogen system, an increase in the concentration of hydrogen ion or a decrease in the concentration of uncharged hydrogen would tend to make the oxidation potential more positive. A decrease in the concentration of hydrogen ion or an increase in the concentration of uncharged hydrogen would tend to make the oxidation potential less positive.

304. Definition of Arbitrary Zero Potential. — In order to compare the oxidation potentials of various systems, it is necessary to have some arbitrarily selected zero potential for a scale of potentials. The zero potential most commonly used in America is the equilibrium potential produced by the hydrogen ion-hydrogen system, in which the activity of hydrogen ion is one and the activity of uncharged hydrogen is that which exists in a solution saturated with hydrogen at one atmosphere of pressure. A platinum electrode in equilibrium with this solution is known as a *normal hydrogen electrode*. The activity of hydrogen ion is one in a 1.2 *M* solution of HCl.[3] If the solution used is molar with respect to hydrogen ion, the activity of hydrogen ion will be slightly less than one and the potential of the electrode will not be exactly zero. This potential will differ so little from zero, however, that in many calculations it can be regarded as equal to zero. It is often convenient to use the concentration of hydrogen ion rather than the activity, and so we shall consider in connection with our problems that a solution saturated with hydrogen gas at one atmosphere and containing one mole per liter of hydrogen ion has a potential of zero.

[3] H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1931.

305. Measurement of Oxidation Potential. — If two normal hydrogen electrodes connected by a salt bridge are attached to
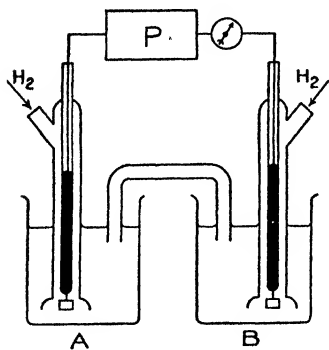
Fig. 57

Cell Consisting of Two Hydrogen Electrodes Connected by a Salt Bridge

a potentiometer equipped with a galvanometer, as shown in Figure 57, no galvanometer deflection will be observed since the electrodes are at the same potential, namely, zero potential. If the hydrogen supply to solution B is diminished so that the concentration of dissolved hydrogen becomes, let us say, one millionth of that required to saturate the solution, the oxidation potential of solution B will be raised to some value above zero which will be indicated in volts by the potentiometer. If, in B, we use a solution saturated with hydrogen but containing much less than one mole per liter of hydrogen ion, its oxidation potential will be negative, the number of volts below zero potential being given by the potentiometer.

In a similar manner, we can compare the potential of the system in the normal hydrogen electrode with that of other oxidant-reductant systems. Thus, let us suppose that the potential of a platinum or gold electrode in a solution containing the ferric-ferrous system is found to be 0.60 volts more positive than the normal hydrogen electrode. Since the potential of the normal hydrogen electrode has arbitrarily been assumed to be zero, it follows that the oxidation potential of the ferric-ferrous system is $+ 0.60$ volts. This relationship is shown in Figure 58.
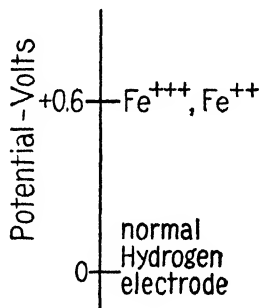
Fig. 58

Comparison of Potential in a Given Solution Containing Ferric and Ferrous Ions with That of the Normal Hydrogen Electrode

By way of further and more detailed illustration, let us consider, in Figure 59, the cell formed when the hydrogen electrode D

immersed in tenth molar hydrochloric acid in B is connected to the normal hydrogen electrode in A by means of the salt bridge S and the potentiometer P. This cell can be considered to be composed of the two half-cells, A and B. The galvanometer G, the cell C to supply an external potential and the key K to close the circuit are connected as shown.

When the potentiometer is adjusted to measure the difference of potential between the two electrodes H and D, the reading obtained is the resultant effect of the following component electromotive forces:

1. The electrode potential e_1 of the normal hydrogen electrode.

2. The electrode potential e_2 of the half-cell B.

3. The potential e_3 across the junction of the electrolyte in the salt bridge and that in the half-cell A.

4. The potential e_4 across the junction of the electrolyte in the salt bridge and that in the half-cell B.

Fig. 59

Circuit for Measuring Oxidation Potential, in Which a Hydrogen Reference Electrode Is Used

The potentials e_3 and e_4, known as *liquid junction potentials* or *contact potentials*, can be calculated from Planck's formula.[4] This, however, is a difficult matter, and since the values of contact potentials are seldom over 0.025 volts and are often much less, we shall regard them as negligible and shall ignore them throughout this work. Neglecting the contact potentials e_3 and e_4, and employing a conventional scheme for the representation of electromotive force combinations, we have:

[4] *Weid. Ann.*, **40**, 581 (1890).

electron flow in external circuit →

$(Pt)H_2(1\ atmosphere)H^+(0.1M) \parallel H^+(1.2M)H_2(1\ atmosphere)(Pt)$

← electron flow in cell

The voltage available for the transfer of electrons in an oxidation-reduction reaction is the difference between e_1 and e_2. It is this difference which we observe by means of the potentiometer. In measuring this difference, an equal and opposite external potential is applied from the cell C. The required external potential is obtained by adjusting the movable contact M until the potential difference between the points M and L is just sufficient to give no deflection of the galvanometer when the key K is closed. If the e.m.f. of C and the resistances LO and LM are known, the potential difference between M and L can be calculated. This value will be equal to the difference between e_1 and e_2. If e_1 is the potential of a normal hydrogen electrode, its value will be zero and the difference of potential between H and D will be equal to e_2.
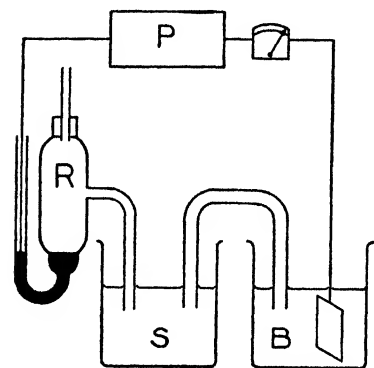
Fig. 60

Circuit for Measuring Oxidation Potential, in Which a Calomel Reference Electrode Is Used

In measuring the oxidation potential of a system, it is not necessary to compare its potential directly with that of a normal hydrogen electrode. It must, however, be compared with a system of known potential. Metallic mercury in contact with a saturated solution of calomel, Hg_2Cl_2, which is normal with respect to potassium chloride, is often used as a reference electrode in potential measurements. This electrode is known as the normal calomel electrode and has a potential of 0.2805 volts at 25°. The partial equation involved is

$$Hg_2^{++} + 2\,e \rightleftarrows 2\,Hg.$$
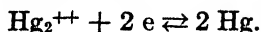
Figure 60 illustrates the use of a calomel electrode R, in measuring the potential of the solution in B by means of the potentiometer

P. When the solution in *B* is of such a nature that it would react with the electrolyte in the calomel cell, the side arm *A* of the calomel cell is not dipped directly into *B* but into an intervening beaker *S* containing an electrolyte which does not react with either the electrolytes in the calomel cell or with the solution in *B*. Let us suppose that we observed by means of the potentiometer that the electrode in *B* is 0.47 volts more positive than the calomel electrode. It follows that the potential of the system in *B* is 0.28 + 0.47 or 0.75 volts more positive than the normal hydrogen electrode. These relationships are diagrammed in Figure 61.
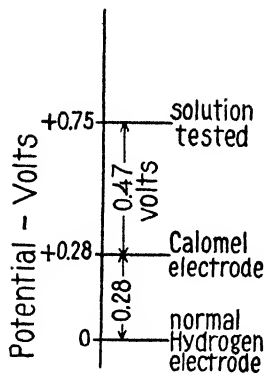
Reference electrodes differing from the normal calomel electrode in that the potassium chloride solution is saturated or tenth normal, are known respectively as the saturated calomel electrode and the tenth normal calomel electrode.

Fig. 61

Comparison of the Oxidation Potential of an Unknown Solution with the Potential of a Normal Calomel Electrode and with That of a Normal Hydrogen Electrode

The potentials of normal, tenth normal and saturated calomel electrodes for 18°, 25° and 30° are given in Table 52.

Table 52

CALOMEL REFERENCE ELECTRODES

Electrode	Potential Volts		
	18°	25°	30°
N KCl | Hg_2Cl_2 + Hg	0.2822	0.2805	0.2792
0.1 N KCl | Hg_2Cl_2 + Hg		0.3334	
Sat. KCl | Hg_2Cl_2 + Hg	0.2511	0.2458	0.2420

306. Calculation of Oxidation Potential. — The magnitude of the equilibrium potential, e, of a system can be arrived at by means of the formula,[5]

$$e = \frac{0.0001983\, T}{n} \log \frac{a_{\text{Oxidant}}^{P}}{a_{\text{Reductant}}^{Q}\, K}$$

in which a_{Oxidant} and $a_{\text{Reductant}}$ are the activities of oxidant and reductant respectively, 0.0001983 is a constant derived from thermodynamic considerations and T is the absolute temperature of the solution. The number of electrons involved in the partial equation of the reaction is represented by n. P and Q are the moles of oxidant and reductant, respectively, appearing in the partial equation of the reaction. K is a constant, characteristic of the system, the value of which is equal to the ratio,

$$\frac{a_{\text{Oxidant}}^{P}}{a_{\text{Reductant}}^{Q}}$$

at which the potential of the system is zero. A complete derivation of this equation is given in the Appendix.

Strictly speaking, the above equation requires the use of activities. When concentrations in moles per liter are used instead of activities in calculating potentials, the results are generally incorrect. The errors involved, however, are usually small enough to permit the use of concentrations in most of the calculations discussed in this text. For the sake of convenience, concentrations will generally be used and, when activities are used, they will be specifically indicated. Using concentrations instead of activities the equation becomes

$$e = \frac{0.0001983\, T}{n} \log \frac{[\text{Oxidant}]^{P}}{[\text{Reductant}]^{Q} K}.$$

Values for K for a number of oxidant-reductant systems are given in Table 53.

[5] W. Nernst, *Z. physik. Chem.*, **4**, 129 (1889). For a very satisfactory exposition and development of Nernst's formula in English, the student is referred to W. C McC. Lewis, "A System of Physical Chemistry," Vol. II, 4th ed., pp. 148–151, Longmans, Green & Co., New York, 1932.

Table 53

MOLAR POTENTIALS AND CONSTANTS AT 25°

System	Reaction	$e°$	K
1. MnO_4^-, MnO_2	$MnO_4^- + 4H^+ + 3e \rightleftarrows MnO_2 + 2H_2O$	+1.59	1.9×10^{-81}
2. MnO_4^-, Mn^{++}	$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{++} + 4H_2O$	+1.5	2×10^{-127}
3. Ce^{++++}, Ce^{+++}	$Ce^{++++} + 1e \rightleftarrows Ce^{+++}$	+1.45	2.9×10^{-25}
4. Au^{+++}, Au	$Au^{+++} + 3e \rightleftarrows Au$	+1.36	9.5×10^{-70}
5. Cl_2, Cl^-	$Cl_2 + 2e \rightleftarrows 2Cl^-$	+1.359	1.02×10^{-46}
6. Cr_2O_7, Cr^{+++}	$Cr_2O_7^= + 14H^+ + 6e \rightleftarrows 2Cr^{+++} + 7H_2O$	+1.3	1×10^{-132}
7. O_2, H_2O	$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	+1.23	5.0×10^{-84}
8. Br_2, Br^-	$Br_2 + 2e \rightleftarrows 2Br^-$	+1.07	5.4×10^{-37}
9. VO_3^-, VO^{++}	$VO_3^- + 4H^+ + 1e \rightleftarrows VO^{++} + 2H_2O$	+0.9	6×10^{-16}
10. Hg^{++}, Hg_2^{++}	$2Hg^{++} + 2e \rightleftarrows Hg_2^{++}$	+0.90	9×10^{-31}
11. Ag^+, Ag	$Ag^+ + 1e \rightleftarrows Ag$	+0.800	2.9×10^{-14}
12. Hg_2^{++}, Hg	$Hg_2^{++} + 2e \rightleftarrows 2Hg$	+0.799	9.1×10^{-28}
13. Fe^{+++}, Fe^{++}	$Fe^{+++} + 1e \rightleftarrows Fe^{++}$	+0.75	2×10^{-13}
14. H_3AsO_4, H_3AsO_3	$H_3AsO_4 + 2H^+ + 2e \rightleftarrows H_3AsO_3 + H_2O$	+0.57	5×10^{-20}
15. I_2, I^-	$I_2 + 2e \rightleftarrows 2I^-$	+0.54	5×10^{-19}
16. $Fe(CN)_6^=$, $Fe(CN)_6^\equiv$	$Fe(CN)_6^= + 1e \rightleftarrows Fe(CN)_6^\equiv$	+0.489	2.8×10^{-17}
17. O_2, OH^-	$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	+0.41	2×10^{-28}
18. Cu^{++}, Cu	$Cu^{++} + 2e \rightleftarrows Cu$	+0.34	3×10^{-12}
19. SbO^+, Sb	$SbO^+ + 2H^+ + 3e \rightleftarrows Sb + H_2O$	+0.21	1.9×10^{-12}
20. Sn^{++++}, Sn^{++}	$Sn^{++++} + 2e \rightleftarrows Sn^{++}$	+0.13	4×10^{-5}
21. Ti^{++++}, Ti^{+++}	$Ti^{++++} + 1e \rightleftarrows Ti^{+++}$	+0.04	2×10^{-1}
22. H^+, H_2	$2H^+ + 2e \rightleftarrows H_2$	0	1
23. Pb^{++}, Pb	$Pb^{++} + 2e \rightleftarrows Pb$	-0.12	1×10^4
24. Sn^{++}, Sn	$Sn^{++} + 2e \rightleftarrows Sn$	-0.14	6×10^4
25. Ni^{++}, Ni	$Ni^{++} + 2e \rightleftarrows Ni$	-0.24	1×10^8
26. Cd^{++}, Cd	$Cd^{++} + 2e \rightleftarrows Cd$	-0.40	3×10^{13}
27. Fe^{++}, Fe	$Fe^{++} + 2e \rightleftarrows Fe$	-0.44	8×10^{14}
28. Zn^{++}, Zn	$Zn^{++} + 2e \rightleftarrows Zn$	-0.76	6×10^{25}
29. Na^+, Na	$Na^+ + 1e \rightleftarrows Na$	-2.71	7.1×10^{45}
30. K^+, K	$K^+ + 1e \rightleftarrows K$	-2.92	2.6×10^{49}

To illustrate the application of the foregoing equation, let us calculate the oxidation potential of the system,

$$I_2 + 2e \rightleftarrows 2I^-$$
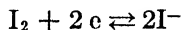
when $[I_2] = 5 \times 10^{-8}$, $[I^-] = 1 \times 10^{-1}$, and when the temperature is 25°. Table 53 gives for this system $K = 5 \times 10^{-19}$. Substituting, we have,

$$e_{I_2, I^-} = \frac{0.0001983\,(273 + 25)}{2} \log \frac{5 \times 10^{-8}}{(1 \times 10^{-1})^2 \times 5 \times 10^{-19}} =$$
$$+ 0.38 \text{ volts.}$$

In calculating the oxidation potential of the system,

$$5e + 8H^+ + MnO_4^- \rightleftarrows Mn^{++} + 4H_2O.$$
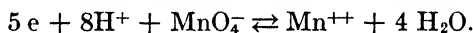
we would have,

$$e_{MnO_4^-, Mn^{++}} = \frac{0.0001983\,T}{5} \log \frac{[H^+]^8\,[MnO_4^-]}{[Mn^{++}] \times K_{MnO_4^-,\,Mn^{++}}}.$$

It is to be noted that since eight hydrogen ions are required for the reduction of one MnO_4^- to Mn^{++}, the equation must include the concentration of hydrogen ion raised to the eighth power. The water formed when this reaction takes place in dilute aqueous solution has scarcely any effect in changing the concentration of water in the solution. Consequently, we consider the concentration of water to be a constant throughout, and include it in the value of K.

307. Molar Potentials. — The equation,

$$e = \frac{0.0001983\,T}{n} \log \frac{[\text{Oxidant}]^P}{[\text{Reductant}]^Q K},$$

may be written,

$$e = \frac{0.0001983\,T}{n} \log \frac{1}{K} + \frac{0.0001983\,T}{n} \log \frac{[\text{Oxidant}]^P}{[\text{Reductant}]^Q}.$$

When the concentrations of the substances involved in a system are molar, the second term on the right becomes zero. The potential under these conditions, known as the *molar potential* of the system, we shall represent by $e°$. Hence,

$$e° = \frac{0.0001983\,T}{n} \log \frac{1}{K},$$

and

$$e = e° + \frac{0.0001983\,T}{n} \log \frac{[\text{Oxidant}]^P}{[\text{Reductant}]^Q}.$$

When this equation is used for the calculation of an oxidation potential, the value of K is not needed, whereas the value of $e°$ must be known. The values of $e°$ for a number of systems may be obtained from Table 53.

By way of illustration of the use of this equation, a solution at 25°, which is tenth molar with respect to ferric ion and one thousandth molar with respect to ferrous ion, would have an oxidation potential of 0.87 volts for,

$$e_{\text{Fe}^{+++},\ \text{Fe}^{++}} = 0.75 + \frac{0.0001983\ (273 + 25)}{1} \log \frac{1 \times 10^{-1}}{1 \times 10^{-3}} = \\ + 0.87 \text{ volts.}$$

Two notable exceptions to our definition of molar potential should be mentioned at this point. These pertain to systems in which one member is a gas and systems in which one member is a metal. They will be dealt with in succeeding paragraphs.

308. *Systems Involving a Gas.* — When one member of a system is a gas, the actual concentration in moles per liter of the gas dissolved in the solution is not used in potential calculations. Since the actual concentration is directly related to the pressure at which the gas is supplied, this pressure may be used to express the concentration of the gas. The molar potential of a system of this sort is the potential existing when all non-gaseous components in solution have concentrations of one mole per liter and when the gaseous member is supplied at a pressure of one atmosphere. The molar potential at 25° for the chlorine-chloride ion system

$$\text{Cl}_2 + 2\,\text{e} \rightleftarrows 2\ \text{Cl}^-$$
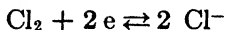
is +1.36 volts. It follows that the potential at 25° of a solution which is tenth molar with respect to chloride ion and to which chlorine gas is supplied at one atmosphere of pressure may be calculated as follows,

$$e_{\text{Cl}_2,\ \text{Cl}^-} = e° + \frac{0.0001983\ T}{2} \log \frac{[\text{Cl}_2]}{[\text{Cl}^-]^2} = 1.36 +$$

$$\frac{0.0001983\ (273 + 25)}{2} \log \frac{1}{(1 \times 10^{-1})^2} = +1.42 \text{ volts.}$$

The potential of the system,

$$2\,e + 2\,H^+ \rightleftarrows H_2,$$

may be obtained from

$$e_{H^+,\,H_2} = e^\circ + \frac{0.0001983\,T}{2} \log \frac{[H^+]^2}{[H_2]},$$

where $[H_2]$ is expressed in atmospheres and e° is the potential of the normal hydrogen electrode and is zero volts. When the H_2 is furnished at one atmosphere of pressure, this equation becomes

$$e_{H^+,\,H_2} = 0 + \frac{0.0001983\,T}{2} \log \frac{[H^+]^2}{1},$$

and it follows that

$$e_{H^+,\,H_2} = 0.0001983\,T \log [H^+].$$

If the solution which is saturated with hydrogen at one atmosphere has a temperature of 25° and contains a hydrogen ion concentration of 0.001 M, then

$$e_{H^+,\,H_2} = 0.0001983\,(273 + 25) \log 10^{-3} = -0.177 \text{ volts};$$

whereas, if the concentration of hydrogen ion is molar,

$$e_{H^+,\,H_2} = 0.0001983\,(273 + 25) \log 1 = 0.$$

The potential of the system,

$$O_2 + 2\,H_2O + 4\,e \rightleftarrows 4\,OH^-,$$
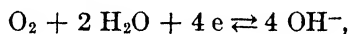
is obtained from

$$e_{O_2,\,OH^-} = e^\circ + \frac{0.0001983\,T}{4} \log \frac{[O_2]}{[OH^-]^4},$$

where $[O_2]$ is expressed in atmospheres. At one atmosphere this becomes

$$e_{O_2,\,OH^-} = e^\circ + \frac{0.0001983\,T}{4} \log \frac{1}{[OH^-]^4} = e^\circ + 0.0001983\,T \log \frac{1}{[OH^-]}.$$

The $[H^+]$ can be used in calculating the potential of this system, for since

$$[H^+]\,[OH^-] = K_{water},$$

and

$$[OH^-] = \frac{K_{water}}{[H^+]},$$

we have

$$e_{\text{O}_2, \text{ OH}^-} = e° + 0.0001983 \ T \log \frac{1}{\dfrac{K_{\text{water}}}{[\text{H}^+]}} = e° + 0.0001983 \ T \log \frac{[\text{H}^+]}{K_{\text{water}}} .$$

It follows that

$$e_{\text{O}_2, \text{OH}^-} = e°_{\text{O}_2, \text{ OH}^-} + 0.0001983 \ T \log \frac{1}{K_{\text{water}}} + 0.0001983 \ T \log [\text{H}^+].$$

If we let

$$e°_{\text{O}_2, \text{ H}_2\text{O}} = e°_{\text{O}_2, \text{ OH}^-} + 0.0001983 \ T \log \frac{1}{K_{\text{water}}},$$

then

$$e_{\text{O}_2, \text{ OH}^-} = e°_{\text{O}_2, \text{ H}_2\text{O}} + 0.0001983 \ T \log [\text{H}^+].$$

The potential equation for systems involving a gas can, of course, be written so as to make use of K rather than $e°$. Thus, for the oxygen-hydroxyl ion system,

$$e_{\text{O}_2, \text{ OH}^-} = \frac{0.0001983 \ T}{4} \log \frac{[\text{O}_2]}{[\text{OH}^-]^4 \ K_{\text{O}_2, \text{ OH}^-}} .$$

309. Systems Involving a Metal. — When one member of a system is a metal, such as the metallic zinc in the system,

$$\text{Zn}^{++} + 2e \rightleftarrows \text{Zn},$$
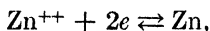
the concentration, in moles per liter, of the metal is considered to be constant and is not used in the potential equation. The potential existing when a pure specimen of the metal is placed in a solution in which the ionic member of the system has a concentration of one mole per liter is taken as the molar potential of the system. Pure zinc in contact with a molar solution of zinc ion at 25° has a potential of -0.76 volts; it follows that the potential existing, when a piece of pure zinc is in equilibrium with a hundredth molar solution of zinc ion at 25°, may be calculated as follows,

$$e_{\text{Zn}^{++}, \text{ Zn}} = e° + \frac{0.0001983 \ T}{2} \log [\text{Zn}^{++}]$$

$$= -0.76 + \frac{0.0001983 \ (273 + 25)}{2} \log 1 \times 10^{-2} = -0.82 \text{ volts.}$$

If the value of e° were not given but the value of K were known, we could calculate the potential from the equation in the form,

$$e_{Zn^{++},\,Zn} = \frac{0.0001983\ T}{2}\log\frac{[Zn^{++}]}{K_{Zn^{++},\,Zn}},$$

where K has a value equal to the concentration of zinc ion which, in equilibrium with pure zinc, would cause the zinc ion-zinc system to have a potential of zero.

If the concentration of the reductant of this system, namely the zinc, were decreased by amalgamation with mercury, the potential of the system would rise. The concentration of zinc ion which would cause the system to have a potential of zero would now be less than when pure zinc was used. Since the concentration of zinc ion producing zero potential has the same value as K, we see that K varies with the purity of the solid zinc. The values of K given in Table 53 for systems in which one member is a metal apply only when the metal is undiluted by impurities.

Potential – Volts

+1.70 ——— Ce⁺⁺⁺⁺, Ce⁺⁺⁺

1.20 volts

+0.50 ——— Fe⁺⁺⁺, Fe⁺⁺

0 ———
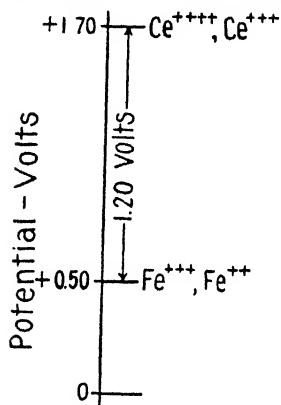
Fig. 62

Potentials Bringing About the Reduction of Ceric Ion and the Oxidation of Ferrous Ion.

310. Potentials and Reaction. — Let us suppose that by comparison with the normal hydrogen electrode we determine the oxidation potential of a solution containing the ceric-cerous system to be +1.70 volts and that of a solution containing the ferric-ferrous system to be +0.50 volts. We have,

$$e_{Ce^{++++},\,Ce^{+++}} = e^\circ + 0.0001983\ T\log\frac{[Ce^{++++}]}{[Ce^{+++}]} = +1.70\ \text{volts}$$

$$e_{Fe^{+++},\,Fe^{++}} = e^\circ + 0.0001983\ T\log\frac{[Fe^{+++}]}{[Fe^{++}]} = +0.50\ \text{volts}.$$

If these two solutions are connected by means of a salt bridge and potentiometer, a difference of potential of 1.20 volts will be observed between the two systems. This is illustrated diagram-

matically in Figure 62.   Let us now consider the change that will take place as a result of this difference of potential when the two electrodes are connected by a wire. The fact that the ceric-cerous potential is higher on the scale of potentials than the ferric-ferrous potential indicates that the ceric-cerous system has a greater tendency to acquire electrons than the ferric-ferrous system. Consequently, the oxidant of the ceric-cerous system, namely, the ceric ion, will gain electrons at the expense of the reductant of the ferric-ferrous system, namely, the ferrous ion. The reaction taking place, therefore, is

$$Ce^{++++} + Fe^{++} \rightarrow Ce^{+++} + Fe^{+++}.$$

Fig. 63

Comparison of the Ceric-Cerous Potential with That of the Ferric-Ferrous Potential at Equilibrium

The consequent decrease of $[Ce^{++++}]$ and increase of $[Ce^{+++}]$ will lower the potential of the ceric-cerous system, and the increase of $[Fe^{+++}]$ and the decrease of $[Fe^{++}]$ will increase the potential of the ferric-ferrous system. When the potential of each system has reached the same value, as illustrated in Figure 63, the following equilibrium will result:

$$Ce^{++++} + Fe^{++} \rightleftarrows Ce^{+++} + Fe^{+++}.$$
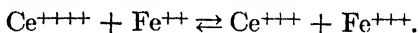
If, to this solution containing the ferric-ferrous system, a large amount of ferric salt is added to increase the concentration of ferric ion, the potential of the ferric-ferrous system will now be higher on the scale of potentials than that of the ceric-cerous system, as shown in Figure 64, and the reaction taking place will be,

Fig. 64

Potentials Bringing About the Reduction of Ferric Ions and the Oxidation of Ferrous Ions

$$Ce^{+++} + Fe^{+++} \rightarrow Ce^{++++} + Fe^{++}.$$

This reaction will reach equilibrium when both potentials reach the same value. Thus, we see that the concentrations of the

components involved are important factors in determining not only the potentials of the systems involved, but also the reaction which takes place.

Two very important principles should be emphasized at this point. They are:

1. When a difference of potential exists between two systems, a reaction will tend to take place in which the oxidant of the system higher on the scale of potentials will obtain electrons from the reductant of the system lower on the scale. In some cases the presence of a catalyst is necessary in order that the reaction may take place with sufficient rapidity to be observed.

2. When both systems involved have the same potential, equilibrium obtains.

These principles apply not only when two systems are in separate containers joined by a salt bridge, but also when both systems are in the same solution.

311. Reversibility of a Reaction. — We have seen that the transfer of electrons between the ceric-cerous and ferric-ferrous systems can be made to proceed in either direction by a proper adjustment of concentrations. We shall consider an oxidation-reduction reaction as reversible when we can effect a change in the direction of electron transfer. In order to reverse the direction of a reaction, it must be possible to change the potentials of either or both of the systems involved sufficiently to cause the system formerly the higher on the scale of potentials to become the lower. As we have seen, one very important way of doing this is by changing the concentration of one or more of the members of the systems involved.

312. The Stoichiometric Potential. — Let us suppose that we have in solution an oxidant-reductant system containing a negligible concentration of reductant and that also in this solution we have a second oxidant-reductant system containing a negligible concentration of oxidant and having a potential lower on the scale of potentials than the first system. Furthermore, let us suppose that stoichiometric quantities of the oxidant of the first system and the reductant of the second system are present. Since the two systems have different potentials, a reaction will take place which at equilibrium may be represented by

$$n_2\,\mathrm{Ox_1} + n_1\mathrm{R_2} \rightleftarrows n_2\mathrm{R_1} + n_1\mathrm{Ox_2},$$
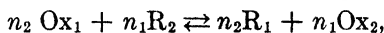
where $\mathrm{Ox_1}$, $\mathrm{R_1}$ and n_1 are the oxidant, reductant and number of electrons per molecule of reacting substance involved in the first system, and $\mathrm{Ox_2}$, $\mathrm{R_2}$ and n_2 are the oxidant, reductant and number of electrons per molecule involved in the second system. If we let P represent the parts per thousand of the stoichiometric quantities of $\mathrm{Ox_1}$ and $\mathrm{R_2}$, which remain unchanged at equilibrium, then $1,000-P$ will represent the $\mathrm{R_1}$ and $\mathrm{Ox_2}$ formed. It follows that we have at equilibrium,

$$\frac{[\mathrm{Ox_1}]}{[\mathrm{R_1}]} = \frac{P}{1,000-P} = \frac{[\mathrm{R_2}]}{[\mathrm{Ox_2}]};$$

also,

$$e_s = e_1^\circ + \frac{0.0001983\,T}{n_1}\log\frac{[\mathrm{Ox_1}]}{[\mathrm{R_1}]} = e_2^\circ + \frac{0.0001983\,T}{n_2}\log\frac{[\mathrm{Ox_2}]}{[\mathrm{R_2}]},$$

where e_s represents the *stoichiometric potential*. Substituting $\dfrac{[\mathrm{R_2}]}{[\mathrm{Ox_2}]}$ for $\dfrac{[\mathrm{Ox_1}]}{[\mathrm{R_1}]}$, we have for system 1,

$$e_s = e_1^\circ + \frac{0.0001983\,T}{n_1}\log\frac{[\mathrm{R_2}]}{[\mathrm{Ox_2}]}$$

or

$$e_s = e_1^\circ - \frac{0.0001983\,T}{n_1}\log\frac{[\mathrm{Ox_2}]}{[\mathrm{R_2}]}.$$

For system 2, we have

$$e_s = e_2^\circ + \frac{0.0001983\,T}{n_2}\log\frac{[\mathrm{Ox_2}]}{[\mathrm{R_2}]}.$$

Multiplying both sides of the equation for system 1 by n_1 and both sides of the equation for system 2 by n_2, we have

$$e_s n_1 = e_1^\circ n_1 - \frac{0.0001983\,T\,n_1}{n_1}\log\frac{[\mathrm{Ox_2}]}{[\mathrm{R_2}]}$$

and

$$e_s n_2 = e_2^\circ n_2 + \frac{0.0001983\,T\,n_2}{n_2}\log\frac{[\mathrm{Ox_2}]}{[\mathrm{R_2}]}.$$

On adding,

$$e_s n_1 + e_s n_2 = e_1^\circ n_1 + e_2^\circ n_2,$$

whence,

$$e_s = \frac{e_1^\circ n_1 + e_2^\circ n_2}{n_1 + n_2}.$$

Let us suppose that the systems involved are

$$1\,e + Ce^{++++} \rightleftarrows Ce^{+++}$$
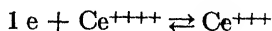
having a molar potential at 25° of $+1.45$ volts and

$$1\,e + Fe^{+++} \rightleftarrows Fe^{++}$$
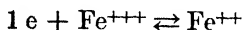
having a molar potential at 25° of $+0.75$ volts, and that we wish to calculate the stoichiometric potential for the equilibrium

$$Ce^{++++} + Fe^{++} \rightleftarrows Ce^{+++} + Fe^{+++},$$
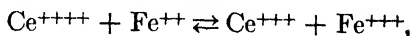
we have at 25°,

$$e_s = \frac{1.45 \times 1 + 0.75 \times 1}{2} = +1.10 \text{ volts}$$

Let us now determine the parts per thousand of Fe^{++} which remain unoxidized at equilibrium.   We have

$$1.10 = +0.75 + 0.0001983\,(273 + 25)\log\frac{[Fe^{+++}]}{[Fe^{++}]}$$

and

$$\log\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{0.35}{0.0591} = 5.92$$

or

$$\frac{[Fe^{+++}]}{[Fe^{++}]} = \frac{10^{5.9}}{1} = \frac{1,000-P}{P};$$

whence,

$$P = 0.0010 \text{ parts per thousand of } Fe^{++} \text{ unoxidized.}$$

We see that by the time equilibrium is reached, ferrous ion has been quantitatively oxidized to ferric ion.

As an illustration of a reaction which is not quantitative, let us suppose that the systems involved are

$$2\,e + Sn^{++++} \rightleftarrows Sn^{++}$$
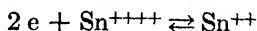
having a molar potential at 25° of $+0.13$ volts, and

$$1\,e + Ti^{++++} \rightleftarrows Ti^{+++}$$
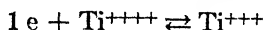
having a molar potential at 25° of $+0.04$ volts.   The stoichiometric potential for the equilibrium

$$Sn^{++++} + 2\,Ti^{+++} \rightleftarrows Sn^{++} + 2\,Ti^{++++}$$
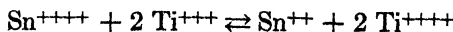
is then

$$e_s = \frac{+0.13 \times 2 + 0.04 \times 1}{3} = +0.10 \text{ volts},$$

and

$$+0.10 = +0.04 + 0.0001983 (273 + 25) \log \frac{[Ti^{++++}]}{[Ti^{+++}]}$$

and

$$\log \frac{[Ti^{++++}]}{[Ti^{+++}]} = 1.02,$$

or

$$\frac{[Ti^{++++}]}{[Ti^{+++}]} = \frac{10^{1.02}}{1} = \frac{1,000 - P}{P};$$

whence,

$$P = 87 \text{ parts per thousand of } Ti^{+++} \text{ unoxidized}.$$

We see that 87 parts per thousand of titanous ion remain un-oxidized and hence the reaction is far from being quantitative at equilibrium. By adding an excess of stannic ion, a more nearly complete oxidation of titanous ion can be effected.

The suitability of a given oxidant-reductant system for the quantitative oxidation or reduction of some other system, when stoichiometric quantities are used, cannot be judged entirely on the basis of the calculated stoichiometric potential. Often complex ion formation, precipitation, evolution of a gas and variations in concentration of the solution play an important part in determining the extent to which an oxidation-reduction reaction proceeds before equilibrium is established. The absence of a suitable catalyst may prevent the reaction from reaching equilibrium. In addition, the values of the constants of many systems are uncertain and, hence, potential calculations for these systems are unreliable.[6]

313. Change of Potential with Progress of Reaction. — In order to study the change in potential of each system involved in a reaction from the beginning of the reaction until the stoichiometric potential is reached, we will consider the reaction

$$Ce^{++++} + Fe^{++} \rightarrow Ce^{+++} + Fe^{+++}.$$

[6] For a very satisfactory discussion of this topic, see Kolthoff and Furman, "Potentiometric Titrations," 2nd ed., John Wiley and Sons, Inc., New York, 1931.

The potential for the ferric-ferrous system may be represented by

$$e_{Fe^{+++},\ Fe^{++}} = e^\circ + 0.0001983\ T \log \frac{[Fe^{+++}]}{[Fe^{++}]}.$$

It is to be noticed that the potential in this case is a function of the ratio of the concentrations of oxidant and reductant and does not depend on the total amount of iron in solution. Let us suppose we have two solutions, one of which is 0.1 M with respect to its total iron content, while the other is 0.001 M, but in each solution half the iron is in the ferric condition while the other half is in the ferrous condition. At 25° the potential in the first solution will be

$$e_{Fe^{+++},\ Fe^{++}} = +0.75 + 0.0001983\ (273 + 25) \log \frac{5 \times 10^{-2}}{5 \times 10^{-2}}$$

$$= +0.75 \text{ volts,}$$

and in the second solution we have

$$e_{Fe^{+++},\ Fe^{++}} = +0.75 + 0.0001983\ (273 + 25) \frac{5 \times 10^{-4}}{5 \times 10^{-4}} = +0.75 \text{ volts.}$$

Table 54

RATIOS OF OXIDANT TO REDUCTANT FOR THE CERIC-CEROUS AND THE FERRIC-FERROUS SYSTEMS AND CORRESPONDING POTENTIALS AT 25°

Ceric-Cerous System			Ferric-Ferrous System		
$\dfrac{[Ce^{++++}]}{[Ce^{+++}]}$	Parts per 1,000 in Reduced Form	Potential, Volts	$\dfrac{[Fe^{+++}]}{[Fe^{++}]}$	Parts per 1,000 in Oxidized Form	Potential, Volts
10,000	0.09999	+1.69	0.0001	0.09999	+0.51
1,000	0.9990	+1.63	0.001	0.9990	+0.57
100	9.901	+1.57	0.01	9.901	+0.63
10	90.91	+1.51	0.1	90.91	+0.69
1	500.0	+1.45	1	500.0	+0.75
0.1	909.1	+1.39	10	909.1	+0.81
0.01	990.1	+1.33	100	990.1	+0.87
0.001	999.0	+1.27	1,000	999.0	+0.93
0.0001	999.9	+1.21	10,000	999.9	+0.99
0.00001	999.99	+1.15	100,000	999.99	+1.05
0.000001	999.999	+1.09	1,000,000	999.999	+1.11

The fact, that for simple ions of the same element the potential is a function of the ratio of the concentrations and not of the total amount, allows us to follow the change of potential with the progress of an oxidation-reduction reaction if we plot the values of the potential as a function of the fraction reduced or oxidized. These values for the ferric-ferrous system are given in Table 54 and are portrayed graphically in Figure 65. As the
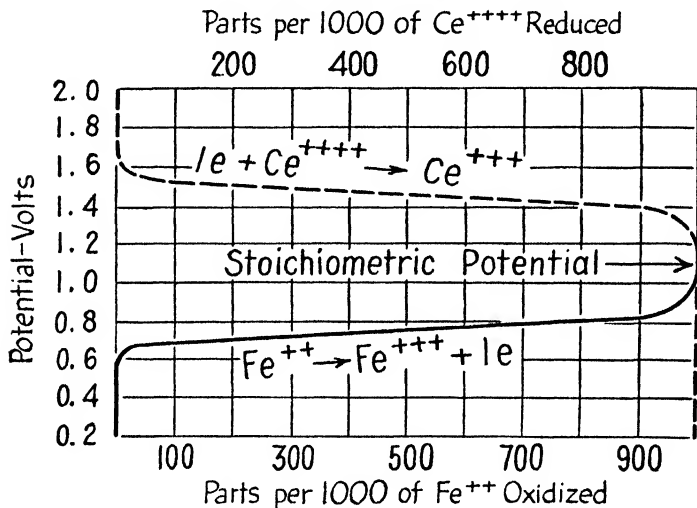
Fig. 65

Ceric-Cerous Potential as a Function of Parts per Thousand of Ceric Ion Reduced; Ferric-Ferrous Potential as a Function of Parts per Thousand of Ferrous Ion Oxidized

oxidation of ferrous ion proceeds, thereby increasing [Fe^{+++}] and decreasing [Fe^{++}], the potential rises as shown by the curve.

In regard to the ceric-cerous system, we have

$$e_{Ce^{++++}, \, Ce^{+++}} = 0.0001983 \; T \log \frac{[Ce^{+++}]}{[Ce^{+++}] \, K_{Ce^{++++}, \, Ce^{+++}}}.$$

The potential of this system is affected, to some extent, by changes in sulfate ion concentration,[7] due probably to the presence of sulfate complexes. Potentials corresponding to the fraction of

[7] Smith and Getz, *Ind. Eng. Chem.*, **10**, 191 (1938).

ceric ion reduced are given in Table 54 and are shown graphically in Figure 65, for solutions which are about molar with respect to sulfate ion.   It is to be noted that as the reduction of ceric ion proceeds, thereby decreasing $[Ce^{++++}]$ and increasing $[Ce^{+++}]$, the potential drops as shown by the curve.

From an inspection of the curves shown in Figure 65 we see that when equivalent quantities of ceric ion and ferrous ion react, both systems involved will have the same potential at the point of intersection of the curves.   This potential is the stoichiometric
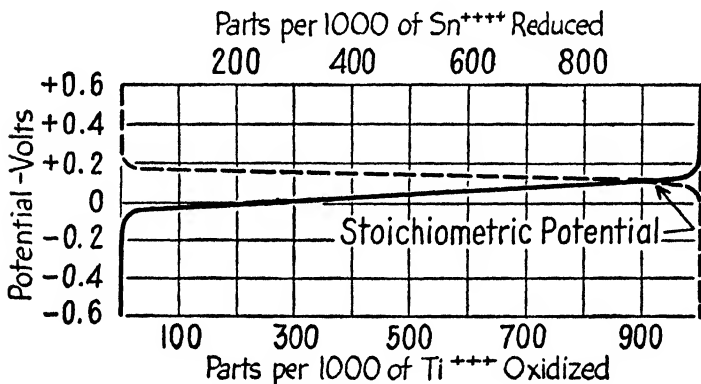
Fig. 66

Stannic, Stannous Potential as a Function of Parts per Thousand of Stannic Ion Reduced;   Titanic, Titanous Potential as a Function of Titanous Ion Oxidized

potential and, when it is attained, equilibrium will result.   The curves show that at equilibrium only an insignificant amount of ferrous ion remains unoxidized.   There is a very important observation to be made here, however, which is that all the iron can never be in the ferric state after oxidation because to obtain such a condition would necessitate the application of an infinite potential, for,

$$e_{Fe^{+++},\,_3Fe^{++}} = e^\circ + 0.0001983 \; T \log \frac{Fe^{+++}}{0} = + \; \infty.$$

An infinite potential is impossible and, therefore, all the iron can never be in the ferric state.   In a similar way, it can be shown

that all the iron can never be in the ferrous state to begin with, because that would demand an infinite negative potential, which is likewise impossible.   It is true that a very large fraction of
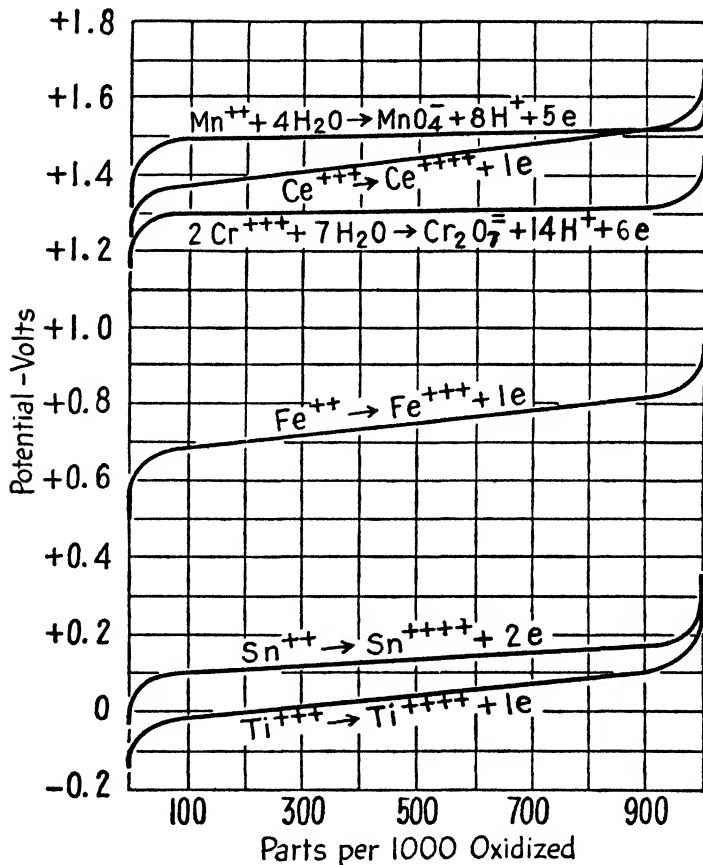
Fig. 67

Oxidation Potential as a Function of Parts per Thousand Oxidized

the iron can be oxidized or reduced, but it is important to bear in mind *that not all of it* can be so affected, because in a titration of ferrous ion to ferric ion we measure only the iron which is in the ferrous condition before titration, and not the total amount

of iron present.   A similar observation applies to other oxidizing and reducing substances.

Figure 66 shows the curves for the reaction of equivalent quantities of titanic and stannous ions.   The reaction which takes place is

$$2\ Ti^{++++} + Sn^{++} \rightarrow 2\ Ti^{+++} + Sn^{++++}.$$
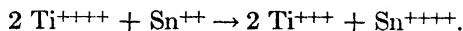
It will be noted, however, that the point of intersection is reached and equilibrium is established when a considerable fraction of the titanous ion remains unoxidized.

Curves for other oxidant-reductant systems are given in Figure 67. The curves of the permanganate-manganous system and of the dichromate-chromic system have been calculated with the assumption that the hydrogen ion concentration remained one mole per liter throughout the reaction.

314. Oxidation-Reduction Titrations. — If we titrate a solution of ferrous ion by means of ceric ion and, during the course of the titration, observe the oxidation potential of the solution by
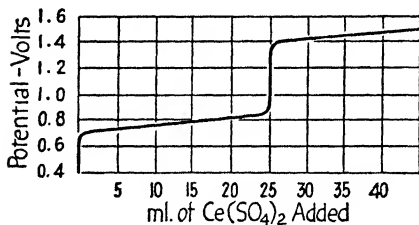
Fig. 68

Titration of Ferrous Ion with Ceric Sulfate Solution

means of the apparatus shown in Figure 59, we obtain values of potential which, when plotted against milliliters of ceric solution added, yield a curve similar to that shown in Figure 68. At the beginning of the titration, the rise of the potential of the ferric-ferrous system produced by the addition of a given volume of ceric solution is small.   When, however, the concentration of ferrous ion has become very small, this rate of rise of potential increases tremendously, as shown by the nearly vertical portion of the curve.   The point of inflection of this portion of the curve is generally close to the stoichiometric point.   The addition of ceric ion beyond the stoichiometric point increases the potential still further, but when the concentration of ceric ion becomes appreciable, the rate at which the potential rises for a given volume of ceric solution added is greatly diminished.   This is shown by

the right-hand portion of the curve. A curve for the titration of a ferrous solution, molar with respect to hydrogen ion, by means of permanganate solution, is shown in Figure 69. In general, we can say that the greater the difference between the molar potentials of the systems involved, the longer and more nearly vertical will be the upright portion of the curve and the easier it will be to locate an end point close to the stoichiometric point.

One method of determining when the point of inflection has been reached in an oxidation-reduction titration is actually to measure the rate of potential change during the titration. Determinations making use of this method are discussed
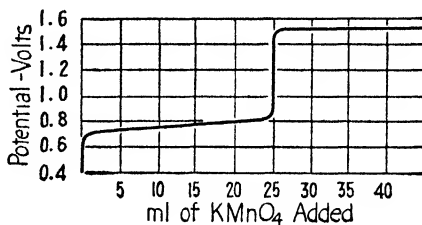
Fig. 69

Titration of Ferrous Ion with Potassium Permanganate Solution

in Chapter XXIV. Another method of locating the stoichiometric point is to arrange matters so that at, or near, the stoichiometric point the solution undergoes a change in appearance. In titrating strongly acid solutions containing reducing ions, with permanganate ion, the pink color produced by a slight excess of permanganate is the end point. In some cases when the systems undergoing reaction do not, of themselves, produce a satisfactory end point, a substance known as an oxidation-reduction indicator may be added in order to produce an end point.

315. Oxidation-Reduction Indicators. — An oxidation-reduction indicator is an oxidant-reductant system which undergoes a marked change in color when oxidized or reduced. By way of illustration, let us suppose that a small amount of such a system is present during the titration of ferrous ion with ceric ion. The increase in potential of the solution to a value sufficiently high to change the indicator from its reduced form to its oxidized form will cause a change in color of the solution. If this end point occurs close to the stoichiometric point, the indicator, if satisfactory in other respects, may be used in the titration. In titrating solutions containing colored ions, such as cobalt and

nickel, with potassium permanganate an oxidation-reduction indicator sometimes produces a clearer end point than that produced by the color of permanganate ion. Some of the more important oxidation-reduction indicators are given in Table 55.

Table 55

Oxidation-Reduction Indicators

Indicator	Color		References
	Oxidized	Reduced	
Phenanthroline Ferrous Ion	Pale Blue $e^* = 1.26$	Red $e = 1.14$	Blau, F., *Monatsh*, **19**, 647 (1898). Walden, Hammett and Chapman, *J. Am. Chem. Soc.*, **53**, 3908 (1931); *ibid.*, **55**, 2649 (1933). Walden, Hammett and Edmonds, *J. Am. Chem. Soc.*, **56**, 57, 350 (1934). Willard and Young, *Ind. Eng. Chem., Anal. Ed.*, **6**, 48 (1934).
Diphenylamine	Violet $e = 0.84$	Colorless $e = 0.76$	Knop, *J. Am. Chem. Soc.*, **46**, 263 (1924). Furman, *Ind. Eng. Chem.*, **17**, 314 (1925). Willard and Young, *J. Am. Chem. Soc.*, **50**, 1334 (1928). Schollenberger, *J. Am. Chem. Soc.*, **53**, 88 (1931). Druce, *Chem. News*, **128**, 237 (1924). Scott, *J. Am. Chem. Soc.*, **46**, 1396 (1924). Mehlig, *J. Chem. Education*, **3**, 824 (1926). Kolthoff, *Chem. Weekblad.*, **26**, 298 (1929). Muchina and Solotarewa, *Z. anal. Chem.*, **104**, 46 (1936).
Diphenylbenzi-dine	Violet $e = 0.84$	Colorless $e = 0.76$	Kolthoff and Sarver, *J. Am. Chem. Soc.*, **52**, 4179 (1930). Cone and Cady, *J. Am. Chem. Soc.*, **49**, 356 (1927). Kolthoff, *Chem. Weekblad.*, **24**, 203 (1927). Sarver and Johnson, *J. Am. Chem. Soc.*, **57**, 329 (1935). Sarver and Fischer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 271 (1935). State, *Ind. Eng. Chem., Anal. Ed.*, **8**, 259 (1936).

Table 55 — *Continued*

Indicator	Color		References
	Oxidized	Reduced	
Diphenylamine Sulfonic Acid	Violet	Colorless	Sarver and Kolthoff, *J. Am. Chem. Soc.*, **53**, 2902 (1931).
	$e = 0.85$	$e = 0.80$	Willard and Young, *Ind. Eng. Chem., Anal. Ed.*, **5**, 154 (1933).
Eroiglaucin A			Knop, *Z. anal. Chem.*, **77**, 125 (1929).
Eriogreen B and			Furman and Wallace, *J. Am. Chem. Soc.*, **52**, 5347 (1930).
Setoglaucin O			Knop, *Z. anal. Chem.*, **85**, 253 (1931).

* Values of e vary somewhat with conditions.

316. *Phenanthroline-ferrous Ion.* — Phenanthroline-ferrous ion indicator consisting of the system,

$$\mathrm{Fe(C_{12}H_8N_2)_3^{++} \rightleftarrows Fe(C_{12}H_8N_2)_3^{+++} + 1\ e,}$$
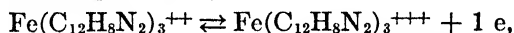
and formed by adding phenanthroline, $C_{12}H_8N_2$, to a solution containing ferrous ion, has been used in titrating iron, arsenic, antimony, thallium, uranium, vanadium, oxalate, ferrocyanide, and peroxide by means of ceric ion. This indicator changes from red to pale blue on being oxidized. The end point potential in the titration of ferrous ion with ceric sulfate solution is 1.2 volts. Phenanthroline-ferrous ion is an organo-metallic complex of high stability. It is highly resistant to destruction by hydrochloric and sulfuric acids in cold solution and is not oxidized to any considerable extent by the air. Copper, cadmium, nickel, cobalt, and zinc form stable complexes with phenanthroline and may prevent the formation of the ferrous complex.

317. *Diphenylamine.* — Diphenylamine yields on oxidation diphenylbenzidine which in turn may be oxidized to diphenylbenzidine violet. The reactions may be written as follows:

diphenylamine   diphenylbenzidine   diphenylbenzidine violet
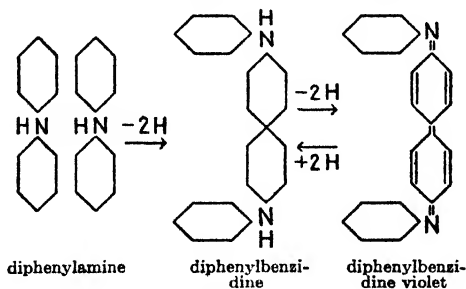
This indicator has been used in titrating ferrous ion with a solution of dichromate ion and in titrating ceric, dichromate, permanganate, and vanadate ions by reduction with a solution of ferrous ion. It has also been used in the volumetric precipitation of zinc by means of potassium ferrocyanide. This method has been discussed in Chapter XIII. This indicator is only slightly soluble in water. It is used in solutions containing sulfuric acid. It changes from colorless to violet on oxidation, the end point potential varying from 0.76 to 0.81 volts in the titration of ferrous ion with dichromate ion.

318. *Diphenylbenzidine.* — Diphenylbenzidine, on oxidation, yields diphenylbenzidine violet, as illustrated above in the second step of the equation for the oxidizing of the diphenylamine indicator. In general, diphenylbenzidine finds its use in the same titrations in which diphenylamine may be used. It is used in solutions containing sulfuric acid. It has the undesirable property of being only slightly soluble in water. Its color change and end point potential are the same as for diphenylamine.

319. *Diphenylamine Sulfonic Acid.* — Diphenylamine sulfonic acid indicator, made by dissolving the sodium or barium salt in water, has the advantage over diphenylamine and diphenylbenzidine of possessing greater solubility in water. The reactions involved in the color change are similar to those which take place in the case of diphenylamine. Among the titrations in which diphenylamine sulfonic acid has been used are the oxidation of iron with ceric ion or with dichromate ion and the reduction of ceric ion and dichromate ion by titrating with ferrous ion. The end point potential for the titration of ferrous ion with dichromate ion is about 0.84 volts.

A consideration of additional properties and details of use of the indicators mentioned will be taken up in connection with the procedures in which they are used.

320. Systems Involving Complex Oxygen Ions. — For many complex oxygen ions it is to be pointed out that the potential depends, not only on the ratio of the concentration of the complex ion to the concentration of the ion resulting from its reduction, but also upon the concentration of hydrogen ion in the solution. To show how the concentration of hydrogen ion enters as a factor,

let us consider the reduction of permanganate ion to manganous ion. The course of this reduction is given by the scheme,

$$5\,e + MnO_4^- + 8\,H^+ \rightleftarrows Mn^{++} + 4\,H_2O,$$
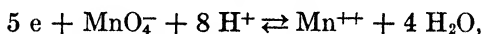
from which it is seen that for each mole of permanganate ion which is reduced to manganous ion, eight moles of hydrogen ion enter into reaction. The change of charge which takes place is found by balancing the charges as represented; for the case in hand, the change of charge is five. We thus have, as the expression for the potential of the permanganate-manganous system,[8]

$$e = \frac{0.0001983\,T}{5} \log \frac{[MnO_4^-][H^+]^8}{[Mn^{++}]\,K_{MnO_4^-,\,Mn^{++}}}$$

where K has a value [9] of about 10^{-127}. The quantity eight appears in the logarithmic part of the formula as the power to which the concentration of hydrogen ion must be raised, because, as shown by the Law of Mass Action, the relationship between the potential and the reacting substances is such that each of the concentrations of the reacting substances must be raised to a power equal to the relative number of moles concerned in the reaction. It is to be noticed in general, in the case of complex oxygen ions which undergo reduction, that the potential varies as the logarithm of some power of the hydrogen ion concentration.

For the reduction of dichromate ion to chromic ion, we have

$$6\,e + Cr_2O_7^= + 14\,H^+ \rightleftarrows 2\,Cr^{+++} + 7\,H_2O$$
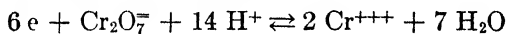
and

$$e = \frac{0.0001983\,T}{6} \log \frac{[Cr_2O_7^=][H^+]^{14}}{[Cr^{+++}]^2\,K_{Cr_2O_7^=,\,Cr^{+++}}},$$

where K is about 10^{-132}.

For the thiosulfate-tetrathionate system,

$$2\,e + S_4O_6^= \rightleftarrows 2\,S_2O_3^=,$$
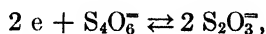
we have for the potential,

$$e = \frac{0.0001983\,T}{2} \log \frac{[S_4O_6^=]}{[S_2O_3^=]^2\,K_{S_4O_6^=,\,S_2O_3^=}}.$$

[8] This relationship, which is really an extended form of Nernst's formula, was first suggested and substantiated by Crotogino, *Z. anorg. Chem.*, **24**, 87 (1900).

[9] Inglis, *Z. Elektrochem.*, **9**, 229 (1903).

It is to be noticed that while the change of charge with respect to the tetrathionate ion is two, *the change of charge is only one with respect to the thiosulfate ion* because two moles of thiosulfate ion are concerned in taking up the two charges.   From the fact that it takes only a moderate potential ($I_2 \rightarrow 2\ I^-$) to oxidize thiosulfate ion quantitatively to tetrathionate ion, it follows that the value of K is fairly large.   Because of its ease of oxidation, thiosulfate ion is widely employed in oxidation-reduction reactions for the titration of liberated or excess iodine in iodimetric processes.   Sodium thiosulfate is the salt which is used as the source of thiosulfate ion.

The oxidation of oxalate ion leads to carbon dioxide according to the scheme

$$C_2O_4^- \rightarrow 2\ CO_2 + 2\ e$$
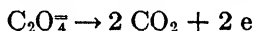
whence, we have for the potential,

$$e = \frac{0.0001983\ T}{2} \log \frac{[CO_2]^2}{[C_2O_4^-]\ K_{CO_2,\ C_2O_4^-}}.$$

From the fact that it takes a very high potential ($MnO_4^- \rightarrow Mn^{++}$) to oxidize oxalate ion quantitatively, it follows that the numerical value of K is small.   Because of its difficulty of quantitative oxidation, oxalate ion is but infrequently employed in oxidation-reduction reactions; almost its sole use is in the standardization of potassium permanganate solutions, and for this purpose a small amount of sodium oxalate is weighed out and dissolved each time as needed.[10]   It might be stated that since the advent of sodium oxalate as the primary standard for potassium permanganate standardization, the tendency has been to base as many methods as possible, either directly or indirectly, on the use of potassium permanganate as the titrating agent.

321. Detailed Study of the Reduction of Permanganate Ion. — The most frequent case that is encountered with respect to permanganate ion is the one in which the reduction proceeds to manganous ion, this transformation corresponding to a transfer of five electrons as shown in the equation,

$$5\ e + MnO_4^- + 8\ H^+ \rightleftarrows Mn^{++} + 4\ H_2O.$$
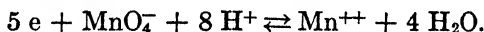
[10] *Nat. Bur. Standards, Circular* No. 40 (1913), Washington, D. C.; Blum, *J. Am. Chem. Soc.*, **34**, 123 (1912); Sörensen, *Z. anal. Chem.*, **42**, 352, 512 (1903); *ibid.*, **44**, 142 (1905).

The reduction can be otherwise conducted, however, so that it will not proceed to manganous ion but will stop at some intermediate state. Thus, under certain conditions, we have the permanganate ion reduced to the acid manganite ion $HMnO_3^-$ which precipitates out as the insoluble manganese dioxide MnO_2. In this transformation the number of electrons transferred is three, as shown in the equation,

$$3\ e + MnO_4^- + 3\ H^+ \rightleftarrows HMnO_3^- + H_2O.$$
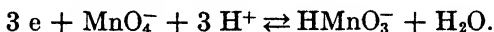
The equation usually given in the literature for this reduction represents the permanganate ion as being directly reduced to manganese dioxide, thus,

$$3\ e + MnO_4^- + 4\ H^+ \rightleftarrows MnO_2 + 2\ H_2O.$$
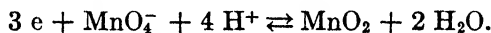
Although this equation gives the correct change of charge, it appears more reasonable to suppose that the permanganate ion is reduced to the acid manganite ion $HMnO_3^-$ (or its amphoteric form Mn^{++++}), the formation of the manganese dioxide resulting from the fact that these ions, which are the ions furnished by manganese dioxide according to the scheme,

$$MnO_2 + 2\ H_2O \rightleftarrows Mn(OH)_4 \begin{cases} Mn^{++++} + 4\ OH^- \\ HMnO_3^- + H^+ + H_2O \end{cases}$$
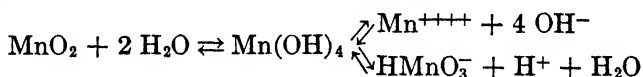
cannot accumulate to any more than the very slightest extent on account of the extremely small solubility product of manganese dioxide.

Again, in the presence of a large excess of fluoride ion, we have the permanganate ion reduced to the trivalent manganic ion Mn^{+++}, the latter uniting with the excess fluorine ion to form the complex ion $MnF_6^{\equiv}$; in this reaction the change of charge is four as shown in the equation,

$$4\ e + MnO_4^- + 8\ H^+ + 6\ F^- \rightleftarrows MnF_6^{\equiv} + 4\ H_2O.$$
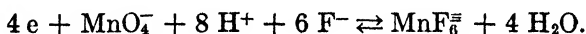
It therefore becomes of primary importance to determine the conditions which in general govern the reduction of permanganate ion. As an aid to our consideration of the problem, let us suppose that we are adding a 0.02 M $KMnO_4$ solution dropwise

to a 0.1 M NaCl solution (Figure 70), and that we have just added the first drop but no more. When the sodium chloride solution is stirred, the pink color of the permanganate ion dis-

0.02M.KMnO4

0.I M.NaCl

Fig. 70

Addition of Potassium Permanganate to a Solution of Sodium Chloride

appears and we know that the latter has been reduced with the oxidation of a certain amount of chloride ion to chlorine. Now it is convenient to consider that the reduction of the permanganate ion takes place stepwise, namely, that the first product of the reduction is the acid manganite ion $HMnO_3^-$, which in turn is reduced to the manganic ion Mn^{+++}, which in turn is reduced to the manganous ion Mn^{++}, so that the course of the reaction is

$$MnO_4^- \rightarrow HMnO_3^- \rightarrow Mn^{+++} \rightarrow Mn^{++}.$$

When the point of equilibrium has been reached, we will have present all of these ions, the relative distribution of their concentrations being such that the respective potentials between the several states of oxidation are all equal, namely, $e_1 = e_2 = e_3$, where

$$e_1 = \frac{0.0001983\ T}{3}\ \log \frac{[MnO_4^-][H^+]^3}{[HMnO_3^-]K_1}, \tag{1}$$

$$e_2 = 0.0001983\ T \log \frac{[HMnO_3^-][H^+]^5}{[Mn^{+++}]K_2}, \tag{2}$$

$$e_3 = 0.0001983\ T \log \frac{[Mn^{+++}]}{[Mn^{++}]K_3}, \tag{3}$$

and where, moreover, the common value of e_1, e_2, and e_3 at the point of equilibrium is the same as that which will exist between the chloride ion and the liberated chlorine, namely, $e_1 = e_2 = e_3 = e_4$ where

$$e_4 = \frac{0.0001983\ T}{2}\ \log \frac{[Cl_2]}{[Cl^-]^2 K}. \tag{4}$$

After the second drop of permanganate solution has been added to the sodium chloride solution and equilibrium has been established, we will have

$$e'_1 = e'_2 = e'_3 = e'_4,$$

where the accents are used to show that it is a different point of equilibrium the potentials of which are being considered. After the third drop has been added, we will have

$$e_1'' = e_2'' = e_3'' = e_4''$$

Now we know from the chemistry of the situation that as the successive quantities of permanganate ion are reduced, the concentration of chlorine is being increased, therefore e_4' will be greater than e_4, e_4'' greater than e_4', etc., the exact manner of increase being portrayed in Figure 71. Consequently,

$$e_1'' > e_1' > e_1$$
$$e_2'' > e_2' > e_2$$
$$e_3'' > e_3' > e_3.$$

Now if we refer to equation (3), we will see that if both e_3 and $[Mn^{++}]$ are increasing, then the $[Mn^{+++}]$ must increase, but the $[Mn^{+++}]$ occurs as the denominator in equation (2), therefore, since e_2 is increasing, it follows that the $[Mn^{++++}]$ is also increasing;

Fig. 71

Potential as a Function of Fraction of Chloride Ion Oxidized

a similar argument shows that the $[MnO_4^-]$ is also increasing. Sooner or later a point will be reached where the $[Mn^{++++}]$ has been built up to a value where the solubility product of manganese dioxide has been exceeded and this compound will precipitate out, as shown by the following equation:

$$Mn^{++++} + 4\,OH^- \rightleftarrows MnO_2 + 2\,H_2O.$$

The concentration of hydrogen ion determines when this precipitation will take place. It can be shown[11] that an increase in

[11] Inglis. *Z. Electrochem.*, **9**, 228 (1903).

the hydrogen ion concentration increases the potential at which MnO_2 precipitates. For hydrogen ion concentrations between $10^{-0.54}$ and $10^{-1.78}$, and for manganous-ion concentrations commonly encountered in quantitative titrations, the potential which must be exceeded in order to bring about precipitation is between 1.21 and 1.42 volts. For higher concentrations of hydrogen ion, the potential which must be exceeded is even higher. The exceeding of this potential not only prevents the reduction of the quadrivalent ion to the manganous ion, but also causes the oxidation of manganous ion to the quadrivalent ion, though still allowing the reduction of permanganate ion to the quadrivalent ion. The quadrivalent ion which is formed after this potential has been reached cannot accumulate in the solution but is precipitated out as manganese dioxide.[12]

Up to the point at which the formation of the manganese dioxide takes place, the change of charge undergone by the permanganate ion is five, all of the change being taken up by the reducing agent; beyond this point, the change of charge is three, part of this change of three being taken up by the reducing agent, the other part being taken up in the oxidation of the manganous ion previously formed during the reduction of the permanganate ion.

These facts lead to a very important consequence, which is, that the point at which the formation of the manganese dioxide takes place must either not be reached until after the end point has been passed, or else must sensibly coincide with the start of a titration.

The reason for this is obvious. For a titration, the amount of substance oxidized must be uniformly proportionate to the amount of oxidizing substance added. If the formation of the manganese dioxide takes place at some intermediate point, part of the titra-

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[12] It is interesting to calculate the potential which corresponds to the establishment of the end point in a permanganate titration as usually effected by the addition of one drop excess of $0.02\,M$ $KMnO_4$. Assuming that the solution has a volume of 500 ml. and a concentration of acid as given, and that about 25 ml. of $0.02\,M$ $KMnO_4$ have been reduced during the titration, we get the following values for 18°:

Concentration of sulfuric acid	$0.25\,M$	$0.05\,M$	$0.01\,M$
Potential (volts)	1.461	1.421	1.376

This shows that any permanganate end point will eventually fade out.

tion will correspond to a change of charge of five; the other part to a change of charge of three, or less, so that there will be no uniform porportionality between the total amount of substance oxidized and the total amount of permanganate added.

The case in which the formation of manganese dioxide does not take place until after the end point has been reached, while throughout the titration the change of charge undergone by the permanganate ion is five, is the case under which fall the great majority of permanganate titrations. This widespread use of the reaction in which permanganate ion is reduced to manganous ion arises from the superiority of its end point and from the fact that it is possible to effect the quantitative oxidation of the great majority of reducing substances at a potential less than $1.21 - 1.42$ volts, the region in which manganese dioxide begins to precipitate out. It is because of the desire to make sure that the reaction shall be one in which the change of charge undergone by the permanganate ion is five that the analyst in titrating with permanganate solution is usually directed to have present a concentration of sulfuric acid of 0.5 M to 1 M. The high concentration of hydrogen ion increases the potential at which the formation of manganese dioxide takes place. The high total concentration of the acid is, in general, sufficient to keep the concentration of hydrogen ion sensibly constant throughout the reaction and also to supply the hydrogen ion used up in the reduction of the permanganate ion.

It will be seen from the ionic equation, $MnO_4^- + 8\,H^+ \rightarrow Mn^{++} + 4\,H_2O$, that, for every mole of permanganate ion which is reduced, there are used up eight moles of hydrogen ion. Thus with the progress of a permanganate titration, there is a continual removal of hydrogen ion from the solution, and consequently if we start with an insufficient concentration of sulfuric acid, the concentration of hydrogen ion will be so diminished that the formation of manganese dioxide will result. Sulfuric acid is chosen because it conveniently furnishes the desired concentration of hydrogen ion, while its anion, SO_4^-, does not act as a reducing agent toward permanganate ion nor as an oxidizing agent toward the substances that are titrated by means of permanganate.

In regard to the use of other acids in place of sulfuric acid, it is essential that any such acid shall, like sulfuric acid, conveniently furnish the desired concentration of hydrogen ion (namely, be highly ionized) while its anion shall not be oxidizable or reducible except with the greatest difficulty. It will be found upon examination, however, that most acids fail to meet one requirement or the other, so that our choice is practically restricted to sulfuric acid. Thus, either nitric or hydrochloric acid could be used so far as building up the concentration of hydrogen ion is concerned, but the former acid furnishes nitrate ion which is a strong oxidizing agent [13] while the latter acid furnishes chloride ion which is a reducing agent with respect to permanganate ion; the use of either of these acids therefore leads to error in a permanganate titration.[14]

The case in which the formation of manganese dioxide takes place at the start of the titration, while throughout the titration the change of charge undergone by the permanganate is three, has only one important titration falling under it, and that is the Volhard method for the determination of manganese.

In this method the stoichiometric relationship is,

$$2 \, MnO_4^- + 3 \, Mn^{++} + 7 \, H_2O \rightarrow 5 \, HMnO_3^- + 9 \, H^+.$$
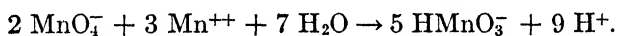
Various metallic ions which can be oxidized in this manner by permanganate ion cannot be determined quantitatively, due to the fact that they form insoluble precipitates with acid manganite ion and are thus removed from the solution before oxidation can be effected. Although manganous ion forms a precipitate with acid manganite ion, the formation of this precipitate can be prevented to a large extent by the addition of zinc ion to the solution, thereby precipitating the acid manganite ion from the solution as the highly insoluble zinc acid manganite. The details are given in §§ 367 and 368.

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[13] For the oxidation potential of nitrate ion, see Ihle, *Z. physik. Chem.*, **19**, 577 (1896).

[14] The same argument applies if the nitrate ion or the chloride ion (or more generally any ion functioning as an oxidizing or reducing agent) is added in the form of a salt and the concentration of hydrogen ion built up by means of sulfuric acid.

322. Balancing of Oxidation-Reduction Equations. — In order to illustrate the method of balancing oxidation-reduction equations, let us take as our first example the reaction, in which ferric ions and stannous ions react to form ferrous ions and stannic ions. First, we write the partial equation for the substance being oxidized and for the substance being reduced, being careful that each equation balances both chemically and electrically. We next multiply each partial equation by numbers so chosen that the number of electrons liberated by the oxidation is equal to the number of electrons taken up by the reduction. The partial equations are then added, the electrons canceling out. These steps are illustrated as follows,

$$
\begin{aligned}
1 \times \qquad & (Sn^{++} \rightarrow Sn^{++++} + 2\ e) \\
2 \times & (1\ e + Fe^{+++} \rightarrow Fe^{++}) \\
\hline
Sn^{++} + & 2\ Fe^{+++} \rightarrow Sn^{++++} + 2\ Fe^{++}.
\end{aligned}
$$
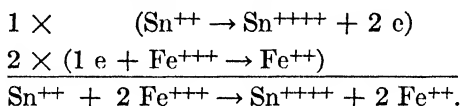
As a further illustration, let us balance the equation for the reaction between permanganate ion, hydrogen ion and ferrous ion to form ferric ion, manganous ion and water. We have,

$$
\begin{aligned}
5 \times \qquad & (Fe^{++} \rightarrow Fe^{+++} + 1\ e) \\
1 \times & (5\ e + 8\ H^+ + MnO_4^- \rightarrow Mn^{++} + 4\ H_2O) \\
\hline
5\ Fe^{++} + & 8\ H^+ + MnO_4^- \rightarrow 5\ Fe^{+++} + Mn^{++} + 4\ H_2O.
\end{aligned}
$$
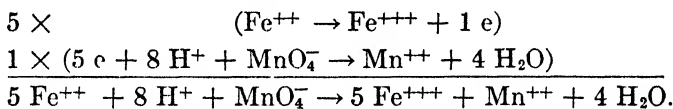
323. Molar Solutions. — There is not much difficulty in making the calculations which are necessary in connection with oxidation-reduction titrations, if we base them upon the changes of charge involved. These calculations can be conveniently carried out when the concentrations of standard solutions are expressed in terms of molarity. A detailed illustration of the calculation of the molarity of a standard solution is given in § 333 and an illustration of the calculation of the per cent of an unknown constituent in a sample, by means of this same standard solution, is given in § 348.

324. Normal Solutions. — For oxidizing and reducing agents, a normal solution is one which contains, per liter of solution, that weight of reagent which would, in accordance with the proper stoichiometric equation, oxidize 126.9 g. of iodide ion or reduce 126.9 g. of iodine. Another way of defining normality as applied

to oxidizing and reducing agents is to say that a normal solution is one which contains, per liter of solution, $\frac{1}{n}$ moles of reagent, when n represents the change of charge which the reagent undergoes in the reaction. Thus, in the case of potassium permanganate solution, when the change of charge is five as illustrated in the following reaction,

$$5 \, e + MnO_4^- + 8 \, H^+ \rightarrow Mn^{++} + 4 \, H_2O,$$
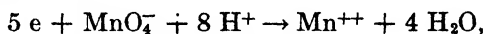
a liter of normal solution will contain

$$\frac{158.03}{5} = 31.61 \text{ g. } KMnO_4.$$

When the change of charge is three, as in

$$3 \, e + MnO_4^- + 3 \, H^+ \rightarrow HMnO_3^- + H_2O,$$
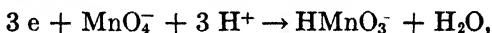
a liter of normal solution will contain

$$\frac{158.03}{3} = 52.68 \text{ g. } KMnO_4.$$

When potassium permanganate solution is used in the presence of a high concentration of fluoride ion, the change of charge is four,

$$4 \, e + MnO_4^- + 8 \, H^+ + 6 \, F^- \rightarrow MnF_6^{\equiv} + 4 \, H_2O,$$
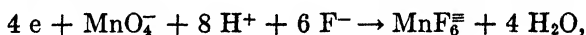
and a liter of normal solution will contain

$$\frac{158.03}{4} = 39.51 \text{ g. } KMnO_4.$$

The criticism put forward in § 157, that the scheme of normality as a basis of definition of concentration is inadequate and should be abandoned, applies *a fortiori* here.

325. Factor Values in Oxidation-Reduction Titrations. — In expressing the concentration of solutions used in oxidation-reduction reactions, it is sometimes convenient to use a system of arbitrary concentration similar to that described in § 160. If we know the factor value of a standard solution, and properly select the size of the sample to be analyzed, we can arrange matters so that 1 milliliter of solution will represent a given per cent of unknown constituent in the sample. Thus, suppose that we have a solution of potassium permanganate 1 ml. of which is the equivalent of 0.006024 g. of iron, and we wish to take such a

weight of iron ore for analysis that each milliliter of permanganate solution used in titration shall correspond to 2% of iron in the ore. The formula is

$$W = \frac{100\,f}{p},$$

where

W = desired weight of sample in grams,

p = % constituent to be represented by 1 ml. of standard solution,

f = number of grams of constituent corresponding to 1 ml. of standard solution.

Whence, upon substituting, we get

$$W = \frac{100 \times 0.006024}{2} = 0.3012 \text{ g.},$$

namely, we take a weight of sample equal to 0.3012 g.

326. Examples.

1. Balance the reactions for each of the following:

(a) Titration of ferrous ion with permanganate.

(b) Titration of arsenous oxide with ceric sulfate solution.

(c) Titration of ferrous ion with dichromate.

(d) Titration of iodine with sodium thiosulfate.

2. The molar potential of the mercuric-mercurous system is + 0.90 volts at 25°. Calculate the value of K for the system.

3. The value of K for the lead ion-lead system is 1.1×10^4. Calculate the molar potential for the system.

4. Calculate the oxidation potential at 25° of a solution which is 0.1 M with respect to ferric ion and 0.001 M with respect to ferrous ion.

5. Write the reaction which takes place at 25° when 50 ml. of a solution which is 0.02 M with respect to ferric ion and 0.002 M with respect to ferrous ion is mixed with 50 ml. of a solution which is 0.002 M with respect to ceric ion, 0.02 M with respect to cerous ion and molar with respect to sulfuric acid. Calculate the potential at equilibrium.

6. Calculate the stoichiometric potential of the titration of ferrous ion with potassium permanganate in a solution which is molar with respect to hydrogen ion.

7. Which will have the more positive potential, a mercury electrode in contact with a solution which is saturated with respect to Hg_2Cl_2 and normal with respect to KCl, or a mercury electrode in contact with a solution which is saturated with respect to Hg_2Cl_2 and saturated with respect to KCl? Explain.

CHAPTER XVI

OXIDIMETRIC METHODS FOR THE DETERMINATION OF IRON

327. Methods of Determining Iron. — Iron is frequently determined oxidimetrically. This element may also be determined gravimetrically by precipitation as ferric-hydroxide with ignition to the oxide, and colorimetrically by forming the thiocyanate complex of the ferric ion. The gravimetric method, however, is open to several objections, chief among which are the difficulties of satisfactorily washing the precipitate and then igniting it to the definite composition, Fe_2O_3. Probably 20 mg. of iron is the upper limit that can be determined gravimetrically with any precision at all. The colorimetric method is good only for very small amounts of iron, say from 0.005 mg. to 0.4 mg. The oxidimetric methods of determining iron include methods in which ferrous ion is titrated to ferric ion by means of potassium permanganate, ceric sulfate, or potassium dichromate. These methods can be applied in the presence of many accompanying elements, which would have to be removed in the gravimetric method. The method involving the use of potassium permanganate is probably the most widely used of the oxidimetric methods. This method is described in the following paragraph.

328. The Determination of Iron by Titration with Potassium Permanganate. — The method of determining iron, by titration with potassium permanganate, can give, under favorable conditions, a precision of 1–2 parts per 1,000 when applied to samples containing 100 mg. or more of iron. The principle of this method is simple enough. The iron, having been brought into solution, is reduced quantitatively by a suitable reducing agent to ferrous ion. The latter is immediately titrated to the ferric condition by means of standard permanganate solution.

329. Some Important Properties of Potassium Permanganate Solution. — Permanganate ion is one of the best oxidizing agents which the analytical chemist has at his disposal for the carrying out of oxidation-reduction reactions. The theory underlying

the behavior of permanganate ion has already been presented at some length in §§ 320 and 321 and it is assumed that the student is familiar with the theory as it has an important bearing in actual practice.   The great practical advantages of permanganate ion are its high potential and its characteristic purple color.   The high potential insures a very small difference between the amount of reducing substance oxidized and the total amount of reducing substance present; the characteristic purple color is so pronounced that only the slightest excess of permanganate ion is necessary to establish an unmistakable end point, one drop (0.05 ml.) of 0.02 M potassium permanganate in a volume of 500 ml. being plainly visible.

The chief disadvantage in the use of potassium permanganate solution, a disadvantage which can be readily overcome, is the necessity of keeping the solution free at all times of even the merest traces of manganese dioxide, because as shown by Morse and co-workers,[1] if manganese dioxide is present, it acts as a catalyst in promoting the formation of more manganese dioxide at the expense of the permanganate ion, thereby bringing about a continuous and increasing lowering in the value of the solution. Furthermore, when the stock bottle of permanganate solution is shaken preparatory to withdrawal of some of the solution, the manganese dioxide will become more or less unevenly suspended, so that successive fillings of pipettes or burettes will have varying amounts of manganese dioxide in them.   Since it takes only a few specks of manganese dioxide to effect the same amount of oxidation as several tenths of a milliliter of 0.02 potassium permanganate solution (the value usually employed), will effect, it means that it is impossible to get concordant or consistent results when manganese dioxide is present.

The manganese dioxide may come from three causes: It may be on the surface of the permanganate salt which is used as the source of permanganate ion even though the salt be an "analyzed" or "C.P." grade; it may come from the reducing action of small amounts of organic matter and ammonia which distilled water usually contains;[2] it may come from the reducing action

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[1] *Am. Chem. J.*, **18**, 411 (1896); *ibid.*, **23**, 313 (1900).
[2] See § 43 for impurities found in distilled water.

of the dirt and organic matter on the inside walls of the stock bottle into which the permanganate solution is to be put.   This third cause, however, need not be encountered at all, as any stock bottle, burette or pipette used for containing a permanganate solution can be and should always be perfectly cleaned beforehand by treatment with dichromate cleaning mixture.   Methods of getting rid of the manganese dioxide from the first and second causes are considered in the following paragraph.

330. Preparation of Potassium Permanganate Solution. — The required amount of potassium permanganate is dissolved in the necessary volume of distilled water contained in a large beaker. The beaker is covered with a watch-glass and the solution is heated to 90°–95° for 2–3 hours, and is then set aside at room temperature for several days so as to insure the complete oxidation of all organic matter.   After this, the permanganate solution is filtered directly into a clean stock bottle using a Gooch crucible with an asbestos mat or a Buchner funnel with an asbestos mat and employing suction.   Under no circumstances should filter paper be used to remove the manganese dioxide.   The filter paper will, it is true, remove the manganese dioxide already present, but as the permanganate solution trickles down the under side of the filter paper, the reducing action of the latter is sufficient to cause the formation of a lot of new manganese dioxide which will go along with the solution.   It is important that the asbestos mat be formed from asbestos which has first been digested with strong nitro-hydrochloric acid and then thoroughly washed with water. It is also advisable, after the mat has been formed in the crucible, to ignite it over the Bunsen burner for several minutes, and then to pass through it a few milliliters of distilled water in order to wash out any small threads that might have become detached.

If a permanganate solution is made up in accordance with the foregoing directions and kept out of direct sunlight, it will keep its value for months.   It is a wise precaution, however, to check this value every now and then by titration against sodium oxalate. If a change of more than 2 parts per 1,000 has taken place, the permanganate solution should be refiltered.   With respect to the use of permanganate solutions, our general caution in regard to the use of standard solutions cannot be too strongly emphasized:

Portions of the solution withdrawn from the stock bottle should never be returned to it. Permanganate solutions are seldom made up to any prescribed exact value because in the attendant dilutions, transference of volumes, etc., the likelihood of conditions favorable to the formation of manganese dioxide would be greatly multiplied. It is usual to make up the solution to an approximate value and then to determine this value exactly by titration. For most purposes a solution which is approximately 0.02 M will be found very convenient. To make up such a solution it is preferable to weigh out an amount of potassium permanganate slightly in excess of that demanded by theory; about 3.20 g. of $KMnO_4$ should be used for each liter of solution rather than 3.16 g. which is the theoretical amount.

331. Standardization of Permanganate Solutions. — There are four principal substances in use for the standardization of permanganate solutions. Stated in order of their preference, the most desirable being put first, they are:

1. Sodium oxalate $Na_2C_2O_4$
2. Ferrous ammonium sulfate hexahydrate $FeSO_4 \cdot (NH_4)_2 SO_4 \cdot 6\ H_2O$ (Mohr's salt)
3. Iron wire
4. Oxalic acid $H_2C_2O_4 \cdot 2\ H_2O$.

In view of the fact that sodium oxalate, because of its many advantages, has practically displaced the other three substances, we will discuss its use in detail and dismiss the other three with only a few observations and references that might be helpful in case it is ever necessary to employ them.

332. Standardization with Sodium Oxalate. — The use of sodium oxalate as a standard was first proposed and adopted by Sörensen;[3] some time later Blum[4] studied quite critically not only the conditions for its preparation as an analytical standard, but also the tests that it should answer, as well as the proper conditions for its use. Shortly after the publication of Blum's work, the Bureau of Standards,[5] Washington, D. C., added this

[3] *Z. anal. Chem.*, **36**, 639 (1897); *ibid.* **42**, 352, 512 (1903); *ibid.* **44**, 141 (1905); *ibid.* **45**, 217 (1906).

[4] *J. Am. Chem. Soc.*, **34**, 123 (1912).

[5] *Nat. Bur. Standards*, *Circular* No. 40. "Sodium Oxalate as a Standard in Volumetric Analysis," Washington, 1913.

very important standard to their list of standards and published a pamphlet setting forth in detail the reasons which led them to this action. Since all this work establishes the great superiority of sodium oxalate as a primary standard in conjunction with standardization of permanganate solutions, every laboratory should be provided with an analyzed grade of sodium oxalate, and in cases demanding extreme care a certified sample obtained from the Bureau should be used.[6]

The conditions to be employed when sodium oxalate is used as a primary standard for permanganate solutions are as follows:[7] In a 400 ml. beaker, dissolve 0.250–0.300 g. of sodium oxalate in 200–250 ml. of hot water (80°–90°) and add 10 ml. of 9 M H_2SO_4. Titrate at once[8] with 0.02 M $KMnO_4$ solution, stirring the liquid vigorously and continuously. The permanganate must not be added more rapidly than 10–15 ml. per minute, and the last 0.5–1 ml. must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The excess of permanganate used to cause the end point color must be estimated by matching the color in another beaker containing the same bulk of acid and hot water. The solution should not be below 60° by the time the end point is reached; more rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot-plate during the titration. The use of a small thermometer as a stirring rod is most convenient in these titrations, as the variation of temperature is then easily observed.

The precision obtained in the titration under these conditions

[6] The Bureau makes a small nominal charge for such samples.

[7] Quoting almost verbatim from Circular of the Bureau of Standards, No. 40, cited above, pp. 10–11.

[8] In regard to keeping this solution of sodium oxalate any length of time before titrating, the words of the Bureau on the stability of stock solutions of sodium oxalate are to the point: "It has been shown that sodium oxalate solutions do not decompose appreciably upon boiling, but that they readily attack glass. This latter effect is noticeable to a lesser degree when the solutions are preserved in glass at the ordinary temperature, giving rise to a precipitate of calcium oxalate which renders difficult the accurate measurement of an aliquot. For this reason and also because of the possible decomposition of sodium oxalate by sunlight, the use of a stock solution for standardizing is not recommended."

is limited only by the apparatus employed. By the use of weight burettes, agreement of duplicates to one part in two thousand can readily be obtained. The precision with volume burettes may be somewhat less than this, depending upon the accuracy of calibration and the care used in the reading of the volume and in maintaining the temperature of the solution constant. In view of the probable warming of the permanganate solution during the titration, the use of weight burettes is recommended whenever a precision better than one part in one thousand is desired.

The absolute accuracy of the results cannot be assumed to be better than one part in a thousand until an exhaustive investigation of the whole subject of volumetric standards is made.

333. Calculation of the Value of Potassium Permanganate Solution. — Let us consider the method of calculating the molarity of a solution of potassium permanganate when sodium oxalate is used as the standard. The reaction involved is balanced as follows:

$$2 \times (5\,e + 8\,H^+ + MnO_4^- \rightarrow Mn^{++} + 4\,H_2O)$$

$$\underline{5 \times \qquad\qquad (C_2O_4^- \rightarrow 2\,CO_2 + 2\,e)}$$

$$16\,H^+ + 2\,MnO_4^- + 5\,C_2O_4^- \rightarrow 2\,Mn^{++} + 10\,CO_2 + 8\,H_2O$$

It follows that

$$2\,MnO_4^- \equiv 5\,C_2O_4^-$$

and

$$2\,KMnO_4 \equiv 5\,Na_2C_2O_4;$$

whence,

$$2,000 \text{ ml. } M \text{ } KMnO_4 \equiv 5 \times 134.0 \text{ g. } Na_2C_2O_4$$

and

$$1 \text{ ml. } M \text{ } KMnO_4 \equiv \frac{5 \times 134.0}{2,000} = 0.3350 \text{ g. } Na_2C_2O_4.$$
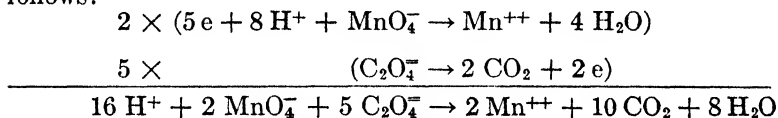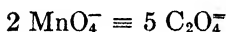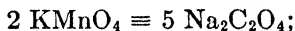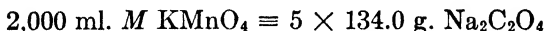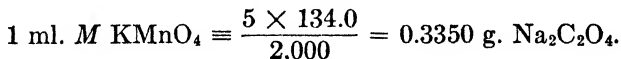
Let us suppose that we have found, as a result of three or more determinations, that 1 ml. of a potassium permanganate solution is equivalent to 0.01033 g. of sodium oxalate. The molarity of the solution is then

$$\frac{0.01033}{0.3350} \equiv 0.03084 \text{ } M.$$

It is often convenient to know the value of the potassium permanganate solution in terms of the weight of iron which 1 ml.

of the solution can convert from the ferrous to the ferric condition. The reaction taking place in a solution which has been made 0.5–1.0 M with sulfuric acid is

$$1 \times (5\,e + 8\,H^+ + MnO_4^- \rightarrow Mn^{++} + 4\,H_2O)$$

$$\underline{5 \times \qquad\qquad (Fe^{++} \rightarrow Fe^{+++} + 1\,e)}$$

$$8\,H^+ + MnO_4^- + 5\,Fe^{++} \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O.$$

It follows that

$$MnO_4^- \equiv 5\,Fe^{++}$$

and we have

$$2\,MnO_4^- \equiv 5\,C_2O_4^- \equiv 10\,Fe^{++}$$

or,

$$2\,KMnO_4 \equiv 5\,Na_2C_2O_4 \equiv 10\,Fe;$$
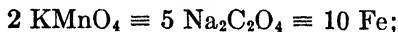
whence,
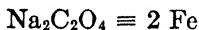
$$Na_2C_2O_4 \equiv 2\,Fe$$

From this relationship and the weight of $Na_2C_2O_4$ equivalent to 1 ml. of the potassium permanganate, we can calculate the weight of iron to which 1 ml. of the solution is equivalent. Thus, for the solution being considered, we have

$$\frac{Na_2C_2O_4}{2\,Fe} = \frac{134.0}{2 \times 55.84} = \frac{0.01033}{X}$$

where $X = 0.008609$ g. Fe equivalent to 1 ml. of $KMnO_4$ solution.

334. Exercise No. 33.   Preparation and Standardization of Potassium Permanganate Solution. — Prepare a liter of approximately 0.02 M potassium permanganate solution by dissolving 3.20 g. of potassium permanganate in sufficient water to make a liter of solution.   Standardize this solution by means of sodium oxalate, running the titration in triplicate.   The average deviation should not exceed 1 part per 1,000.

335. Standardization with Ferrous Ammonium Sulfate Hexahydrate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$. (Mohr's Salt). —When freshly prepared, this salt has the composition as given, but upon standing, the iron in it undergoes oxidation, and some of the water of hydration is given off, with the net result that one cannot be sure of the ferrous content of iron unless the salt is freshly made. Directions for its preparation and use will be found in Olsen.[9]

[9] Olsen, J. C., "Quantitative Chemical Analysis," p. 300, cited in § 11.

336. Standardization with Iron Wire. — This standard was formerly in quite general use before the advent of sodium oxalate. The objections to it are mostly on the score that it is almost impossible to obtain pure iron, the following impurities being always present to greater or less extent:

Silicon	Phosphorus
Sulfur	Carbon

The first three impurities can be determined separately and correction applied accordingly; the fourth impurity can also be determined and correction applied but there is still a further and much more important effect to be considered with respect to the carbon because some of this element will be combined with the iron in the form of some carbide, of which cementite Fe_3C is the most important. When the iron is dissolved in acid, the cementite produces an unsaturated hydrocarbon which acts as a reducing agent toward the permanganate. The error introduced from this source may be very considerable because 1 mg. of carbon (as cementite) will produce enough hydrocarbon to reduce as much permanganate as corresponds to 27.5 mg. of iron. Olsen states [10] in this regard "titrations of solutions of iron wire have been made which indicate as much as 104% of metal in the wire if calculated on the assumption that the only reducing substance present is ferrous iron." To eliminate this error, dissolve the iron in sulfuric acid and then oxidize the hydrocarbons by adding permanganate solution in slight excess to the hot solution of the iron sulfate; the iron is afterward reduced to the ferrous condition by passing through a Jones reductor; it is then ready for titration.

337. Standardization with Oxalic Acid $H_2C_2O_4 \cdot 2 H_2O$. — The principle of using this compound is the same as that of using sodium oxalate, namely, to furnish a definite source of oxalate ion. The objection to its use as a primary standard is that it is not possible to keep or weigh this compound without its losing water, owing to the fact that its vapor pressure is considerably in excess of the partial pressure of water vapor ordinarily existent in the air at room temperatures. Attempts to dry the di-hydrate to a definite composition by keeping in desiccators where the

[10] Olsen, J. C., "Quantitative Chemical Analysis," p. 294, cited in § 11.

atmosphere has a known humidity are not satisfactory. If oxalic acid must be used as an oxidimetric standard for potassium permanganate solutions, a 0.05 M solution of it should be prepared and standardized alkalimetrically by titration against standard sodium hydroxide solution, using phenolphthalein as an indicator; then 25 ml. portions of the acid solution should be measured out, and the conditions established for the titration of oxalate ion, as described in § 332. This whole procedure, however, is a very roundabout affair and should only be employed as a matter of expediency.

338. Methods of Reduction of Ferric Ion. — There are four chief methods in use for the quantitative reduction of ferric ion to ferrous ion. These methods involve the use of one of the following,

1. Metallic zinc	3. Sulfite ion
2. Stannous ion	4. Sulfide ion

The choice of the particular reductant depends largely on the accompanying elements which may be present and which may be susceptible to changes in their states of oxidation. Table 56

Table 56

Effects of Various Reductants on Iron, Titanium and Vanadium

	$Zn + H_2SO_4$	Sn^{++}	S^-	SO_3^-
Fe^{+++}	Fe^{++}	Fe^{++}	Fe^{++}	Fe^{++}
VO_3^-	$\begin{cases} VO^{++} \\ V^{+++} \\ V^{++} \end{cases}$	$\begin{cases} VO^{++} \\ V^{+++} \\ V^{++} \end{cases}$	VO^{++}	VO^{++}
Ti^{++++}	Ti^{+++}	no action	no action	no action

shows the respective behaviors of the several reductants toward ferric ion and toward the ions of vanadium and titanium, two elements frequently encountered with iron. In the absence of vanadium and titanium, the best reductant to use for ferric ion is zinc. We will now describe the use of the several reductants.

339. Reduction with Zinc. — It was formerly the practice to add a few grams of granulated zinc to the iron solution contained in a flask so arranged as to allow for the replacement of its atmosphere of air by an atmosphere of carbon dioxide during the reduction of the ferric ion. Any excess zinc was dissolved by introducing more acid, after which the ferrous ion was titrated.

The foregoing technique is seldom employed today on account of the radical improvement due to C. Jones,[11] who developed a device which is now generally spoken of as a *Jones reductor*. The details of its construction and operation will now be considered.

340. The Jones Reductor. — Jones showed that ferric ion could be quantitatively reduced to ferrous ion if the iron solution was passed slowly enough through a column of granulated zinc, the column having certain specified dimensions. The important features of such a device are shown in Figure 72. The reductor consists of a cylindrical glass tube having a length of about 22 cm. and an internal diameter of about 1.8 cm. At its top end it is enlarged so as to form a reservoir of about 100-ml. capacity; at its lower end it is constricted and drawn out into a smaller tube about 15 cm. long and 0.6 cm. internal diameter. This small tube, provided with a stop-cock as shown, is passed through a one-hole rubber stopper that will fit tightly in

Fig. 72

Jones Reductor

the mouth of a stout-walled suction flask. The Jones reductor can be used only in conjunction with suction. It is always advisable to have the suction flask of the Jones reductor connected not directly to the suction pump but to an intervening suction flask in series
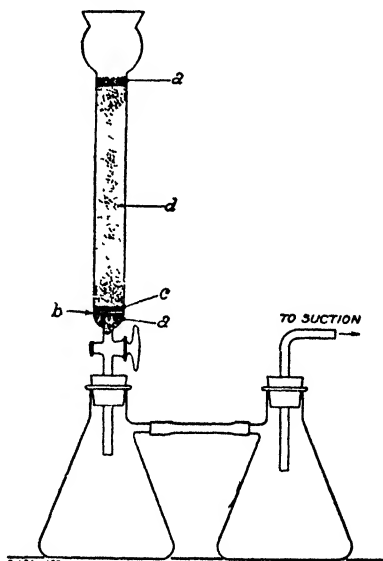
[11] *Trans. Am. Inst. Min. Eng.*, **17**, 414 (1889); *Chem. News*, **60**, 93 (1889).

with the pump, so that, if any water backs up from the pump, it will not spoil the determination.

To prepare the reductor, a small plug of glass wool a is placed in the bottom of the main tube, allowing it to extend slightly into the smaller tube without packing too snugly; on top of the glass wool is placed a small perforated porcelain plate b such as is used in a Gooch crucible; then a layer of asbestos fiber c is added to the depth of 1–2 mm. Next the main tube is filled with amalgamated zinc d[12] up to within 2 cm. of the floor of the reservoir; and finally, a layer of glass wool or asbestos fiber about 2 cm. thick is placed on top of the amalgamated zinc. After the reductor has been thus prepared, about 500 ml. of distilled water is passed through it (using suction), turning off the stop-cock when the reservoir is half full of water. The reductor is now ready for use except that a blank (§ 341) must first be run to insure that it is working properly.

Amalgamated zinc possesses an advantage over ordinary zinc in that it allows a shorter reductor to be used owing to its more rapid action. It also tends to diminish the amount of zinc oxidized to zinc ion by hydrogen ion due to the fact that mercury is a poor catalyst for the reaction in which gaseous hydrogen is evolved. To prepare the amalgamated zinc, 3–5 g. of metallic mercury are weighed out and placed in a large beaker. About 20 ml. of 8 M nitric acid is added, warming slightly until action starts. After the mercury has dissolved, about 400–500 ml. of water is added, then 250 g. of granulated zinc, which is fine enough to pass a 20 mesh sieve, but not fine enough to pass a 30 mesh sieve. The zinc particles are stirred continuously for several minutes, and then examined carefully to make sure that all are amalgamated as shown by their bright luster. The solution is poured off and the zinc is washed with water several times by decantation until all the acid is removed. If the amalgamated zinc cannot be put in the reductor at once, it should be covered with distilled water in the meanwhile.

Before proceeding to discuss the use of the reductor, a few pertinent remarks will fit in here. Whenever a reductor is not

[12] Amalgamated zinc was first proposed by A. J. McKenna, see Mellor, p. 190 of reference given in § 11.

in use, the column of zinc must be kept entirely covered with distilled water. If a reductor is used very frequently, the column of zinc will settle, owing to the consumption of the zinc by the chemical action. When this settling occurs, more amalgamated zinc should be added. If a reductor stands unused for any length of time, the zinc will become encrusted with zinc oxide and will not allow liquid to pass readily; in such a case the reservoir should be filled with 1 M sulfuric acid (never under any circumstances use nitric acid) and the suction should be turned on at the same time. Once the acid begins to percolate through the zinc, it will take only a short time for the complete clearance of the column.

To use the reductor, the solution containing the ion to be reduced should have a volume of about 150 ml. and a concentration of *sulfuric acid of about one* [13] *molar*, and unless otherwise specified should be at room temperature. This solution is passed through the reductor at the rate of 35–40 ml. per minute. As soon as the reservoir is nearly emptied of the solution, 200 ml. of one molar sulfuric acid are added to the reservoir and passed through the reductor at the same rate that the solution was. The acid, in turn, is followed by 100 ml. of distilled water, which is drawn down to within a short distance of the top of the zinc, when the flow is stopped by turning off the stop-cock. The function of the acid is to wash the column clear of solution; the function of the water is to wash out the acid. The total contents of the suction flask are immediately titrated without transference to any other vessel.

341. Cautions in Use of Jones Reductor. — There are two very important cautions to be observed in the use of the Jones reductor. They are as follows:

1. While a reductor is being used, or while it is standing idle, the column of zinc must never be allowed to become exposed to the air.

2. Before running any determination with a reductor, it must be ascertained that the reductor is working properly. This test is made by running a blank.

[13] This concentration need not be exact; anywhere between 0.9 and 1.2 M will answer.

These two cautions will now be considered more fully.

Exposure to Air. — If the column of zinc becomes exposed to the air at any time, the air will become entrained with the descending column of liquid. When this happens the oxygen in the air is reduced to hydrogen peroxide according to the reaction:

$$O_2 + 2\,H^+ + Zn \rightarrow H_2O_2 + Zn^{++}.$$
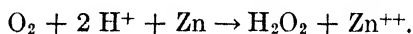
The hydrogen peroxide passes into the solution which is to be subsequently titrated, and since it is oxidized by permanganate ion according to the equation

$$H_2O_2 \rightarrow 2\,H^+ + O_2 + 2\,e,$$
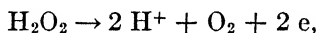
it will cause a noticeable error even though only a few tenths of a milligram of hydrogen peroxide is formed. In point of fact, an error equivalent to 0.5 ml. of 0.02 M permanganate may be easily introduced from this cause. Exposure to air may also lead to the formation of basic salts of zinc which may prevent the ready flow of liquid through the reductor.

Running a Blank. — The running of a blank consists in passing through the reductor 350 ml. of 1 M sulfuric acid which should be at room temperature, and following this by 100 ml. of water (in brief, paralleling the successive volumes, acidity, rate of flow, etc., of a determination). The total contents of the suction flask are then immediately titrated with standard permanganate solution. If the reductor is working properly, it will require only 1–2 drops of 0.02 M $KMnO_4$ to establish a satisfactory end point; if it requires more permanganate solution than this, a second blank with a fresh portion of acid and water must be run, and so on until a satisfactory blank is obtained. If several determinations are to be run in series, or the reductor is to be used continuously all day, one satisfactory blank will suffice. A new blank, however, should always be run each new day that a reductor is used. When a reductor is freshly prepared, it often requires the running of four or five blanks before a satisfactory blank is obtained. If it is impossible to get a satisfactory blank after repeated trials, then there is something wrong with the zinc or with the sulfuric acid; probably an appreciable amount of iron is present.

342. Exercise No. 34.   Preparation of a Jones Reductor and Determination of the Reductor Blank. — Prepare a Jones reductor according to the foregoing directions and then obtain a satisfactory blank.

343. Reduction with Stannous Ion. — Stannous ion is used as a reducing agent particularly in the determination of iron in iron ores; the salt of tin which is used as the source of stannous ion is stannous chloride.   As this salt undergoes hydrolysis to a very large degree, it is necessary to dissolve it in 3 M hydrochloric acid in order to get and keep it in solution; for iron ore analysis, a 1 M solution of the salt in 3 M hydrochloric acid is generally employed.   Stannous ion has a weak reducing potential; it is therefore necessary, when using it to reduce ferric ion quantitatively, to have it present at the completion of the reduction in greater concentration than that which corresponds to the stoichiometric point of the reaction,

$$2 \; Fe^{+++} + Sn^{++} \rightleftarrows 2 \; Fe^{++} + Sn^{++++}.$$
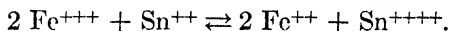
This necessary concentration of stannous ion will be insured if 2–3 drops excess of 1 M stannous chloride solution are added to the iron solution contained in a volume of 30–40 ml.   Before titration, however, the excess stannous ion must be removed. This removal is accomplished through the agency of mercuric ion.   For the practical details see § 351.

344. Reduction with Sulfide Ion. — The most widely used reducing agent for the determination of iron in rock analyses is sulfide ion because of the fact that, in rocks, titanium and vanadium will almost invariably be found in addition to the iron.   The reducing potential of sulfide ion is affected tremendously by the concentration of hydrogen ion existent in the solution at the time. This circumstance arises from the fact that the potential naturally depends upon the concentration of the sulfide ion; hence, any factor which affects this concentration will affect the potential, and we have already seen in §§ 126 and 185 how greatly the concentration of sulfide ion varies with change in the concentration of hydrogen ion.   The maximum acidity which can be employed with sulfide ion and still allow its quantitative reduction of ferric ion is that established by a concentration of sulfuric acid

equal to 0.4 M. If a higher acidity than this is employed, the reduction will be incomplete; if a lower acidity is employed, the reduction will be complete but it will not be possible to get rid of all the excess hydrogen sulfide in the solution by the means commonly employed of passing a rapid stream of carbon dioxide through the boiling solution — therefore, results will be high in this case. The test for the complete removal of the hydrogen sulfide from the solution is to expose a piece of lead acetate paper to the escaping gas. The test is most delicate when the flask is provided with a two-hole stopper fitted with inlet and outlet tubes of glass. If the outside opening of the outlet tube is small, the concentration of the escaping steam and gas contributes to the sharpness of the test. For the details of this method, see § 462.

345. Reduction with Sulfite Ion. — Sulfite ion is sometimes employed as a reducing agent, although it is really an inferior substitute for sulfide ion. The reducing potential depends naturally upon the concentration of sulfite ion existent in the solution; but since sulfurous acid is a very weak acid, the concentration of sulfite ion is affected tremendously by the concentration hydrogen ion of the solution. If the solution is much more acid than corresponds to a $pH = 5.0$, the reduction of the ferric ion will not be complete; on the other hand, if the acidity is made much less than this, there arises the difficulty that ferric hydroxide may precipitate. "The direct use of a solution of sulfur dioxide or an alkaline sulfite[14] is inadmissible unless these have been freshly prepared, for after a lapse of time they contain other oxidizable bodies than sulfurous acid or a sulfite. The sulfur dioxide is best obtained as wanted by heating a flask containing a solution of sulfur dioxide, or of a sulfite to which sulfuric acid has been added. The expulsion of the last trace of sulfur dioxide is said to be accomplished more effectively by boiling with simultaneous passage of a rapid current of carbon dioxide for a few minutes at the last than by boiling alone." "It is not advisable to depend upon the sense of smell;[15] the escaping gas is tested by passing it through dilute sulfuric acid containing a few drops of 0.02 M

[14] Quoting Hillebrand, p. 186 of reference given in § 11.
[15] Quoting Treadwell-Hall, p. 553 of reference given in § 11.

KMnO₄ solution. If the latter is not decolorized at the end of two or three minutes the excess of sulfur dioxide has been removed." The reduced solution is then cooled in an atmosphere of carbon dioxide and titrated.

346. Reduction with Silver Reductor. — Recently metallic silver has been proposed as a reductant for ferric ion. Its use necessitates the presence of chloride ion. The reaction involved is as follows,

$$Fe^{+++} + Ag + Cl^- \rightarrow Fe^{++} + AgCl.$$

This reaction is carried out in a reductor similar to a Jones reductor. An advantage claimed for the silver reductor is that any vanadium present is reduced definitely to V^{+++} whereas in the Jones reductor it is indefinitely reduced. Other advantages claimed are that the silver reductor gives no blank and operates satisfactorily when small concentrations of nitric acid are present. For details of construction and use see Walden, Hammett and Edmonds, *J. Am. Chem. Soc.* **56,** 350 (1934).

347. Exercise No. 35. Determination of Iron in a Mixture of Ferrous and Potassium Sulfates.[16]— It is presupposed that the student has already prepared a standard potassium permanganate solution and a Jones reductor. A satisfactory reductor blank must be obtained. This can be done to advantage in the present case while the sample of unknown is being dissolved. Weigh out a sample of about 1 g. and transfer it to a 250 ml. beaker, add 50 ml. of water and 15 ml. of 18 M H_2SO_4 and heat to 60° or so, until dissolved. Dilute with 100 ml. of water. It is important to digest the sample with concentrated acid first to effect solution, and then dilute; if the sample is treated directly with dilute acid, it probably will not go into solution. The reason for this is that basic salts may be present and basic salts, whether of iron or other element, require a high concentration of hydrogen ion and digestion at elevated temperatures, 60°–95°, to effect their solution. After diluting, pass through the reductor, following with 150 ml. of 1 M H_2SO_4 and 100 ml. of distilled water. Titrate at once with the standard permanganate solution and report the

[16] Samples of the above mixtures ranging in content of iron from 12 to 20% may be used. Standardized solutions of ferrous ammonium sulfate will also serve for the determination.

percentage of iron on the dry basis. The method of calculating the iron content of the sample is given in the following paragraph.

348. Calculation of Iron Content of Unknown Sample. — Let us suppose that in titrating the iron in 1.1002 g. of unknown sample containing 1.50% moisture, 30.20 ml. of 0.03084 M solution of $KMnO_4$ were used, and that it is required to calculate the per cent of iron in the sample on the dry basis. On balancing the equation for the reaction taking place during the titration, we obtain

$$8H^+ + MnO_4^- + 5\,Fe^{++} \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O,$$
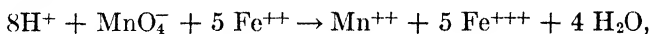
from which it follows that
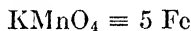
$$KMnO_4 \equiv 5\,Fe$$

and the weight of iron present is obtained as follows,

$$30.20 \text{ ml. } 0.03084\ M\ KMnO_4 \equiv \frac{5 \times 55.84 \times 30.20 \times 0.03084}{1,000}$$
$$\equiv 0.2600 \text{ g. of Fe}$$

and the per cent of iron on the dry basis is

$$\frac{0.2600 \times 100}{1.1002 \times (1-0.015)} = 24.00\%\ Fe.$$

In calculating the weight of iron in the sample, the iron value of the potassium permanganate solution may be employed. Let us suppose that

$$1 \text{ ml. of } KMnO_4 \equiv 0.008608 \text{ g. of Fe,}$$
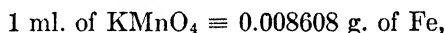
then the weight of iron present is

$$0.008608 \times 30.20 = 0.2600 \text{ g. of Fe.}$$

349. The Zimmerman-Reinhardt Method of Determining Iron in an Iron Ore. — When chloride ion is present during the titration of ferrous ion with permanganate ion, some of the permanganate solution may be used in oxidizing chloride ion. This oxidation may proceed as shown in the following reaction:

$$16\,H^+ + 2\,MnO_4^- + 10\,Cl^- \rightarrow 2\,Mn^{++} + 5\,Cl_2 + 8\,H_2O.$$
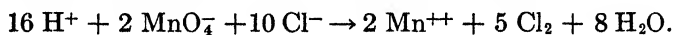
An error is introduced into the results when chloride ion is oxidized, for only part of the permanganate solution run from the burette is used in oxidizing ferrous ion.

When the dissolving of an iron sample necessitates the use of hydrochloric acid or stannous chloride, and thereby yields a solution containing chloride ion, the procedure for determining iron must provide for either the removal of chloride or for the obtaining of conditions under which the error due to its presence is not excessive. The method of removing chloride ion by the addition of H_2SO_4, followed by heating to drive off HCl, is discussed by Willard and Furman.[17] We shall now consider the Zimmerman-Reinhardt method which provides for the obtaining of conditions under which ferrous ion can be titrated in the presence of chloride ion without excessive error.

In this method, after dissolving the sample, the iron is reduced to ferrous ion by means of an excess of stannous ion, according to the reaction,

$$2\ Fe^{+++} + Sn^{++} \rightarrow 2\ Fe^{++} + Sn^{++++}.$$
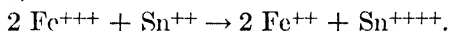
The excess of stannous ion is then removed by adding mercuric ion; thus,

$$Sn^{++} + 2\ Hg^{++} + 2\ Cl^- \rightarrow Sn^{++++} + Hg_2Cl_2 \downarrow$$
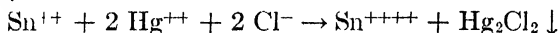
The ferrous ion is then titrated with standard permanganate solution, the oxidation of chloride ion being prevented by *"preventive solution."* This solution will be considered in the following paragraph.

350. Theory of "Preventive Solution."—"Preventive solution" is 2.0 M with respect to H_3PO_4, 2.0 M with respect to H_2SO_4 and 0.3 M with respect to $MnSO_4$. Its use allows the titration of ferrous ion by permanganate ion in the presence of small concentrations of chloride ion. The presence of 10 ml. of "preventive solution" in a volume of 600–700 ml. makes possible the titration of iron when 10 ml. of 12 M HCl or its equivalent are present. Larger concentrations than this of chloride ion cannot be taken care of by "preventive solution," even though far greater quantities of the latter are employed.

The potential necessary to cause the quantitative oxidation of ferrous ion to ferric ion (where the oxidation is accomplished in a dilute sulfuric acid solution) is about 0.860 volts. This is shown by the following experiment:

[17] Willard and Furman, p. 176 of reference given in § 11.

Experiment I. — 25.00 ml. of approximately 0.1 M ferrous ammonium sulfate and 10 ml. of 18 M sulfuric acid were added to 125 ml. of water, and passed through the Jones reductor; this was followed with 150 ml. of 1 M sulfuric acid and 100 ml. of water. The total volume of 400 ml. was titrated at once with 0.02614 M potassium permanganate solution in an atmosphere of carbon dioxide; the temperature was maintained at 25° by means of a thermostat; the potentials were obtained by means of the combination,

$$\text{Hg (Hg}_2\text{Cl}_2 \text{ sat. KCl–sat.)}|\text{KCl–sat.}|(\text{Fe}^{++}, \text{Fe}^{+++}) \text{ Pt.}$$
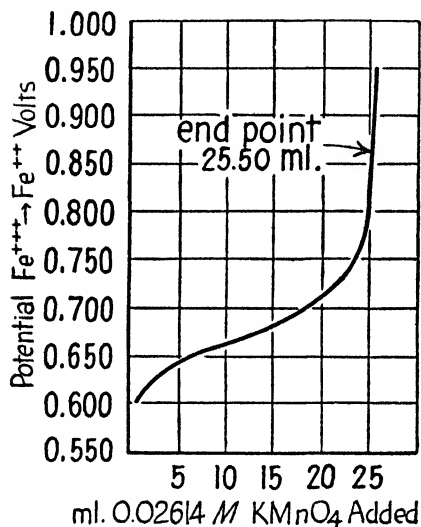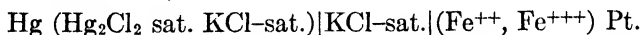
ml. 0.02614 M KMnO$_4$ Added	Potential Fe^{+++}, Fe^{++} (Volts)
1.0	0.592
1.5	0.602
2.5	0.617
5.0	0.638
15.0	0.683
20.0	0.707
23.0	0.732
23.5	0.739
24.0	0.746
25.5	{ 0.860 End point
25.8	0.976

Fig. 73

Titration of Ferrous Ion with Potassium Permanganate in the Absence of Chloride Ion

These results are shown graphically in Figure 73.

If the oxidation of ferrous ion to ferric ion is attempted in the presence of chloride ion, the successive potentials for corresponding amounts of potassium permanganate solution added are about 25 millivolts higher than the potentials obtained when the titration is conducted in the presence of sulfate ion, provided the concentration of hydrogen ion in the two cases is the same. It will also

be found that when the end point is reached in the presence of chloride ion, a larger amount of permanganate solution will have been used than was used when sulfate ion was the anion. This is shown by Experiment II.

Experiment II. — When the same experimentation was followed as in Experiment I, with the exception that for each milliliter of 18 *M* sulfuric acid used in Experiment I, 1 ml. of 12 *M* hydrochloric acid was substituted in Experiment II, the following potentials were obtained:

ml. 0.02614 *M* KMnO$_4$ Added	Potential Fe^{+++}, Fe^{++} (Volts)
1.0	0.604
2.0	0.623
5.0	0.653
10.0	0.679
15.0	0.702
20.0	0.729
23.0	0.765
24.0	0.767
24.5	0.779
25.0	0.807
25.6	0.879
25.9	{ 0.898 { End point
26.3	0 959
28.0	1.236
29.0	1.281
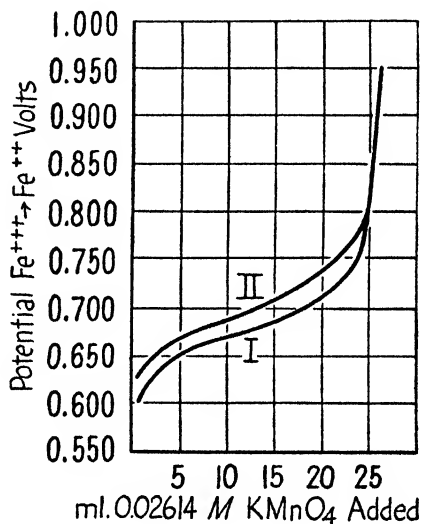
Fig. 74

Titration of Ferrous Ion with Potassium Permanganate in the Presence of Chloride Ion

These results are shown graphically in Figure 74.

Now the excess of permanganate solution which is used when chloride ion is present represents the amount of chloride ion which is oxidized. This amount will naturally be greater, the greater the value of the oxidizing potential existent during the titration.

Right here the velocity with which the permanganate ion is reduced enters as a factor. If the reduction were instantaneous,

the potentials existent throughout the course of the titration would be the equilibrium potentials (Curve II); but since it takes more or less time for each drop of permanganate solution to be reduced, we have a sudden increase of potential above that given by the equilibrium curve and then an adjustment toward the next equilibrium point, and so on. Thus the actual potentials are considerably in excess of the equilibrium potentials, the amount of excess being determined by the rate at which permanganate ion is being reduced relative to the rate at which it is being added.

The problem, then, of titrating ferrous ion in the presence of chloride ion is to arrange matters, if possible, so that not only the end point shall be reached at a minimum potential, but also so that the momentary values of the potential shall be kept as low as possible.

The preventive solution accomplishes both these aims. The phosphate ion which it furnishes ties up the ferric ion, as fast as it is formed, in the form of the highly undissociated ferric phosphate complex, thereby lowering the potential necessary to cause the oxidation of the remaining ferrous ion; the manganous ion acts as a catalyst in speeding up the reduction of the permanganate ion, thereby keeping the actual potentials very close to the equilibrium potentials. These effects are shown clearly by the results obtained in Experiment III.

Fig. 75

Titration of Ferrous Ion with Potassium Permanganate in the Presence of Chloride Ion and Preventive Solution

Experiment III. — This was performed under the same conditions as Experiment II, except that 10 ml. of "preventive solution" was added to the ferrous solution before the latter was passed

through the Jones reductor. The following potentials were obtained:

ml. 0.02614 M KMnO$_4$ Added	Potential Fe^{+++}, Fe^{++} (Volts)
2.0	0.592
3.0	0.597
5.0	0.609
10.0	0.631
15.0	0.651
20.0	0.676
23.0	0.708
24.0	0.740
24.5	0.784
25.2	0.840
25.5	0.860 End point
26.0	0.900

These results are shown graphically in Figure 75.

By comparing the titration curves of Experiments II and III (Figure 75), it is clear that preventive solution lowers the potential necessary for the oxidation of ferrous ion. ' The catalytic effect of manganous ion in speeding up the reduction of permanganate ion, and thereby keeping the actual potentials very close to the equilibrium potentials, is inferred from the fact that it took exactly the same volume of permanganate solution to reach the end point (25.50 ml.) in both Experiments I and III. It is consequently inferred that during Experiment'III the potentials at no time reached a value where chloride ion was oxidized by the permanganate solution.

351. Exercise No. 36. Determination of Iron in Iron Ore by the Zimmerman-Reinhardt Method.[18]— The sample of ore which is taken for analysis should be carefully sampled and finely ground. This is an essential preliminary to the analysis. A determination of moisture in the sample should be made and included in the report, and the temperature at which the moisture is driven off should also be stated (105°–110°). The percentage of iron should be calculated to the dry basis.

[18] *Ber*, **14,** 779 (1881); *Chem.-Ztg.*, **13,** 323 (1889).

Solution. — In most cases solution of an iron ore can be effected by treatment of it with hot 12 M hydrochloric acid and 1 M stannous chloride, provided the ore is ground to a fineness of 100 mesh.   If a small white residue remains, it is usually assumed to be free from iron and is disregarded; if the residue is large or colored, as is the case particularly with magnetites, it will contain iron and must be fused with sodium carbonate, etc., and the iron determined.   Limonites contain organic matter and must be previously ignited with access of air, otherwise they are soluble with difficulty, and, moreover, the organic matter, unless destroyed, is likely to reduce permanganate ion, thereby causing high results.

Weigh accurately about 0.300 g. of the ore sample and transfer to a small beaker.   Add about 10 ml. of 12 M hydrochloric acid and about 2–3 ml. of 1 M stannous chloride solution (dissolved in 3 M hydrochloric acid).   Cover the beaker with a watch-glass and heat for 5–10 minutes, or until no further action occurs.   If the solution turns yellow, showing the presence of ferric ion, add more stannous chloride solution drop by drop until colorless. Examine the undissolved residue carefully.   If pure white, it may be assumed that the iron is all in solution and the reduction and titration may be carried out as described later.   In this case, it is not necessary to filter the solution.

If the residue contains iron, decant the solution through a 7 cm. filter paper into a small beaker and transfer the residue to the filter, using as little water as possible, and wash with a small amount of water containing a little hydrochloric acid.[19]   Place the filter containing the residue in a platinum crucible and ignite in the usual way to burn off the filter paper.   Mix the residue with five to six times its weight of anhydrous sodium carbonate and fuse for about 30 minutes with the Bunsen burner. Spread the fused mass around the inside walls of the crucible by holding the latter in a pair of tongs and rotating the crucible while the mass is cooling.   Place the crucible in a small beaker and add about 15 ml. of water, cover with a watch-glass and heat for a

[19] It is necessary to remove all tin salts from this residue as the next operation to which it is to be submitted is a sodium carbonate fusion in a platinum crucible.

few minutes.   Add very carefully, while the beaker is still covered, about 10 ml. of 12 M hydrochloric acid in small portions.   Heat until the reaction is complete, then remove the crucible, washing any solution from it into the beaker with water.   Without filtering off the silica, precipitate the iron as ferric hydroxide by the addition of a slight excess of ammonium hydroxide solution.   Heat to boiling, filter through a small (7 cm.) filter paper and wash with hot water.   Reject the filtrate.   Dissolve the ferric hydroxide through the filter paper by pouring upon it small portions of hot 6 M hydrochloric acid.   Wash the paper with water and add the filtrate and washings to the solution containing the major portion of the iron obtained from the first treatment of the ore.

There are two important reasons why, in the above procedure, the hydrochloric acid solution of the fused mass cannot be added directly to the main solution of the sample.   (1) The high concentration of chloride ion which would result would diminish the concentration of mercuric ion by forming complex mercury salts and would thereby establish a potential at which mercurous ion would be reduced to elemental mercury by the excess stannous ion.   If a precipitate of black elemental mercury forms, the determination is valueless because mercury in a finely divided condition is rapidly oxidized by permanganate ion.   (2) There is always a small amount of platinum dissolved during the sodium carbonate fusion.   If this finds its way into the main iron solution, it will be reduced to platinous ion when stannous chloride is subsequently added for the purpose of reducing ferric ion.   Platinous ion will give a very intense yellow color to the solution, similar to that of ferric ion.   As this color will persist in the presence of an excess of stannous ion, the disappearance of the similar color due to the presence of ferric ion cannot be recognized.   On the other hand, if the iron in the hydrochloric acid solution of the fused mass is precipitated as described, the platinum salt passes into the sodium chloride filtrate which is rejected.

Reduction. — The resulting solution should now have a volume not greater than 30 ml.; if the volume is greater than this, the solution must be evaporated.   If the solution is colorless, showing excess of stannous ion, add to the solution, which must be kept

hot (70°-90°), 0.1 M potassium permanganate solution, dropwise, until the color due to ferric ion appears. Now add 1 M stannous chloride solution drop by drop until the color due to ferric ion is removed and *then add not more than two drops in excess.* The excess of stannous ion is necessary to insure the quantitative reduction of the ferric ion:

$$2\ Fe^{+++} + Sn^{++} \rightarrow 2\ Fe^{++} + Sn^{++++}.$$
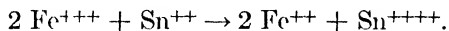
Wash down the sides of the beaker with cold water and dilute with cold water to about 75 ml. The temperature of the solution should not be above 25° after dilution. Stir the solution and, at the same time, add quickly 10 ml. of 0.25 M mercuric chloride solution. A saturated solution of mercuric chloride will answer since, at room temperature (20°-25°), it has a concentration of mercuric chloride of about 0.25 M. The excess of stannous ion is removed by oxidizing it to stannic ion through the agency of mercuric ion:

$$Sn^{++} + 2\ Hg^{++} + 2\ Cl^- \rightarrow Sn^{++++} + Hg_2Cl_2 \downarrow\ .$$
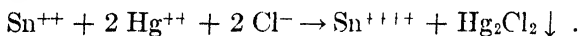
The mercurous ion is practically completely removed as solid Hg_2Cl_2. If the concentration of Sn^+ is too great, its reducing potential will be sufficient to cause not only the reduction of mercuric ion to mercurous ion, but also the simultaneous reduction of mercurous ion to elemental mercury, a circumstance which would vitiate the determination because, as already stated, elemental mercury in a finely divided condition is oxidized by permanganate ion.

Titration. — If a silky white precipitate of mercurous chloride forms, pour the solution into about 600 ml. of water to which 10 ml. of "preventive solution" have been added, and titrate at once with standard approximately 0.02 M permanganate, stirring the solution vigorously. The end point is not the permanent pink color obtained in the absence of chloride, but is the first pink coloration seen throughout the whole solution; this coloration fades in a few seconds. From the data thus secured and the data from the moisture determination, calculate to the dry basis the percentage of iron in the ore.

352. The Determination of Iron by Titration with Ceric Sulfate Solution. — Ceric sulfate solution serves as an oxidizing

agent in many reactions by virtue of the reduction of ceric ions to cerous ions. This change is represented as follows:

$$1\,e + Ce^{++++} \rightarrow Ce^{+++}.$$
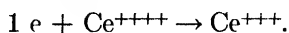
In some respects, ceric sulfate solution is superior to potassium permanganate solution as a standard solution in oxidimetric titrations. It possesses greater stability, it does not appreciably oxidize chloride ion under the usual conditions of analysis, and it undergoes only one valence change, namely, the one illustrated above. The use of ceric sulfate solution, however, is limited to use with acid solutions and generally requires the addition of an indicator due to the fact that the yellow color of the ceric solution is not sufficiently distinct to give a sharp end point.

In the determination of iron by titration with ceric sulfate solution, the iron must previously be reduced to ferrous ion by some suitable method. During the titration, the iron is oxidized to ferric ion by the ceric ion in accordance with the equation,

$$Fe^{++} + Ce^{++++} \rightarrow Fe^{+++} + Ce^{+++}.$$
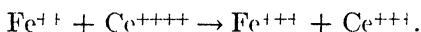
As previously mentioned, in §§ 312 and 313, this reaction is quantitative at the stoichiometric potential. The indistinctness of the color change taking place at the equilibrium point necessitates the use of a small quantity of an oxidation-reduction indicator. Diphenylamine sulfonic acid or phenanthroline ferrous ion may be used for this titration. The use of these indicators in the determination of iron necessitates the addition of phosphoric acid to keep the ferric ion concentration low during the titration by forming the complex ferric phosphate ion. In this way, the oxidation potential of the ferric-ferrous system is lowered sufficiently to prevent the ferric ion from oxidizing the indicator before the end point is reached.

Diphenylamine Sulfonic Acid Indicator. — A 0.01 *M* solution of this indicator may be obtained by dissolving 0.64 g. of diphenylamine barium sulfonate in 180 ml. of water. The barium ion is then precipitated as barium sulfate by adding 20 ml. of 2 *M* H_2SO_4. The clear liquid is then decanted from the precipitate. (See §§ 315 and 319.)

Phenanthroline-ferrous Ion Indicator. — This indicator contains the phenanthroline-ferrous ion, the formula of which is

$Fe(C_{12}H_8N_2)_3^{++}$. It can be made by dissolving in a 0.025 M solution of $FeSO_4$ an amount of phenanthroline monohydrate equivalent to the iron in the solution. The preparation of 100 ml. of indicator solution requires the addition of 1.49 g. of phenanthroline monohydrate (see §§ 315 and 316).

The preparation and standardization of ceric sulfate solution will now be considered.

353. Preparation and Standardization of Ceric Sulfate Solution. — Ceric sulfate solution may be prepared by dissolving ceric ammonium sulfate, $Ce(SO_4)_2 \cdot 2 (NH_4)_2SO_4 \cdot 2 H_2O$, in dilute sulfuric acid.

This solution may be standardized against arsenous oxide, using phenanthroline-ferrous ion as indicator. When this method is used, a catalyst is required. A small amount of a solution which is 0.01 M with respect to osmium tetroxide and 0.05 M with respect to sulfuric acid may be used as the catalyst.[20] The proper performance of this catalyst requires that the solution contain no chloride ion. On oxidation, the color of this indicator changes from pink to pale blue. When one or two drops of indicator are added and 0.1 M ceric sulfate solution is used in the titration, the volume of ceric sulfate solution required to oxidize the indicator is negligible. The reaction involved in the titration is

$$2\ Ce^{++++} + H_3AsO_3 + H_2O \rightarrow 2\ Ce^{+++} + H_3AsO_4 + 2\ H^+.$$
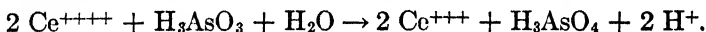
It follows that
$$4\ Ce^{++++} \equiv 2\ H_3AsO_3 \rightleftharpoons As_2O_3.$$

Other standards in use for ceric sulfate solution are sodium oxalate, electrolytic iron and potassium ferrocyanide.

The details for the preparation of ceric sulfate solution and its standardization against arsenous oxide are given in the following paragraph.

354. Exercise No. 37. Preparation of Ceric Sulfate Solution and Standardization against Arsenous Oxide. — Prepare a 0.1 M solution of ceric sulfate by dissolving 64 g. of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2 H_2O$ in 500 ml. of M H_2SO_4 and diluting to one liter with water.

Weigh out into 400 ml. beakers triplicate samples of dry As_2O_3

[20] Willard and Young, *J. Am. Chem. Soc.*, **55**, 3260 (1933).

weighing between 0.15 and 0.20 g. Add 25 ml. of molar NaOH solution. Warm gently and stir till the arsenous oxide is dissolved. Add 100 ml. of water, followed by 20 ml. of 3 M H_2SO_4. Add two drops of a 0.01 M solution of OsO_4 and two drops of 0.025 M phenanthroline ferrous ion indicator and titrate with approximately 0.1 M ceric sulfate solution. At the end point, the color changes from pink to pale blue. Calculate the molarity and the iron value of the ceric sulfate solution.

355. Exercise No. 38. Determination of Iron in an Iron Ore by the Ceric Sulfate Method. — Perform the grinding, sampling, dissolving and reducing operations in this determination exactly as given in the Zimmerman-Reinhardt method of determining iron, described in § 351. After adding the mercuric chloride solution to oxidize the excess stannous ion, transfer the solution to a 400 ml. beaker containing 100 ml. of water. Add 10 ml. of 12 M HCl and sufficient water to bring the volume to 250 ml. Add 10 ml. of phosphoric acid having a specific gravity of 1.35 and then 0.3 ml. of 0.01 M diphenylamine sulfonic acid.[21] Titrate the solution with 0.1 M ceric sulfate solution. The end point is a change from colorless to deep purple. From the results obtained and the results of a moisture determination performed on a separate portion of the sample, calculate the per cent of iron on the dry basis.

356. The Determination of Iron by Titration with Potassium Dichromate Solution. — Potassium dichromate solution may be used as an oxidizing agent in oxidimetric titrations due to its reduction to chromic ion, as illustrated in the following equation,

$$6e + 14\,H^+ + Cr_2O_7^- \rightarrow 2\,Cr^{+++} + 7\,H_2O.$$
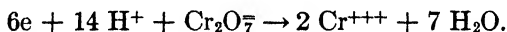
Potassium dichromate solution is superior in some respects to potassium permanganate solution. It possesses greater stability, and it does not appreciably oxidize chloride ion under the usual conditions of analysis. A potassium dichromate solution of known concentration can be prepared by dissolving a carefully weighed quantity of purified $K_2Cr_2O_7$ in a very carefully measured volume of solution, thereby avoiding the necessity of standardizing. The use of potassium dichromate solution, however, is limited to acid solutions and requires the addition of an indicator.

[21] Willard and Young, *J. Am. Chem. Soc.*, **50**, 1334 (1928).

The potassium dichromate used in this method should possess a high degree of purity, having been freed from chlorides and sulfates by recrystallization. The better grades of potassium dichromate which are supplied for analytical purposes usually conform to a very high degree of purity with the exception that they generally contain a little water. To get rid of this moisture, it is best to heat the salt in a platinum crucible to a point just above its fusion point which is 396°. Care should be taken to exclude all dust and organic matter. After cooling, the fused salt should be crushed to a powder in an agate mortar and should then be placed in a glass-stoppered bottle to protect it from dust.

In the determination of iron by titration with potassium-dichromate solution, the iron must previously be reduced to ferrous ion by some suitable method. During the titration, the iron is oxidized to ferric ion by the dichromate ion in accordance with the equation,

$$6 \ Fe^{++} + Cr_2O_7^= + 14 \ H^+ \rightarrow 6 \ Fe^{+++} + 2 \ Cr^{+++} + 7 \ H_2O.$$
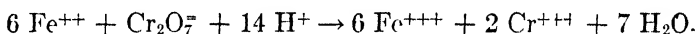
At the stoichiometric potential ferrous ion is quantitatively oxidized. Diphenylamine sulfonic acid [22] may be used as the indicator, producing at the end point a color change from green to purple with a negligible indicator blank. When this indicator is used in the titration of ferrous ion, the addition of phosphoric acid is required to prevent the ferric-ferrous potential from rising sufficiently to oxidize the indicator before the end point is reached.

The details of preparation of standard potassium dichromate solution will now be considered.

357. Exercise No. 39. Preparation of Standard Potassium Dichromate Solution. — Weigh out carefully to a tenth of a milligram approximately 4.9 g. of C.P. $K_2Cr_2O_7$. Dissolve it in water and make up carefully to one liter in an accurately calibrated volumetric flask. Calculate the molarity and the iron value of the solution.

358. Exercise No. 40. The Determination of Iron in an Iron Ore by the Potassium Dichromate Method. — Perform the grinding, sampling, dissolving, reducing, and diluting operations exactly as directed in § 351. After bringing the volume to 250

[22] Sarver and Kolthoff, *J. Am. Chem. Soc.*, **53**, 2902 (1931).

ml., add 20 ml. of phosphoric acid having a specific gravity of 1.35. Then add 0.3 ml. of 0.01 M diphenylamine sulfonic acid and titrate the solution with approximately 0.017 M $K_2Cr_2O_7$ solution. The end point is a change from green to purple. Run a blank to eliminate errors due to impurities in the reagents used. From the results obtained and the results of a moisture determination performed on a separate portion of the sample, calculate the per cent of iron on the dry basis.

359. Examples.

1. 29.98 ml. of $KMnO_4$ solution is equivalent to 0.3010 g. of $Na_2C_2O_4$. Calculate the iron value and the molarity of the $KMnO_4$ solution.

2. 40.24 ml. of a $KMnO_4$ solution having an iron value of 0.008334 was required for the titration of the iron in an ore. Calculate the weight of iron in the sample.

3. 31.09 ml. of 0.05111 M $KMnO_4$ solution was required to titrate the iron in a 2.0104 g. sample of ore containing 2.51% moisture. Calculate the per cent of iron in the ore on the moisture free basis.

4. 30.13 ml. of $KMnO_4$ solution was required to titrate 0.3005 g. of $Na_2C_2O_4$. 42.68 ml. of the same $KMnO_4$ solution was required to titrate the iron in a 2.0105 g. sample of ore containing 1.12% moisture. Calculate the per cent of iron in the ore on the moisture free basis.

5. 32.60 ml. of a solution of ceric sulfate was required to titrate 0.1412 g. of As_2O_3. Calculate the molarity and the iron value of the ceric sulfate solution.

6. 26.07 ml. of 0.1255 M solution of ceric sulfate solution was required to titrate the iron in a sample of ore. Calculate the weight of Fe in the sample.

7. A solution of potassium permanganate contains 3.156 g. $KMnO_4$ per liter. Find its value in terms of iron, ferrous oxide, and ferric oxide.

$$\text{Ans.} \quad 1 \text{ ml.} \equiv \begin{cases} 0.005576 \text{ g. Fe.} \\ .007174 \text{ g. FeO.} \\ .007973 \text{ g. } Fe_2O_3. \end{cases}$$

8. 4.8211 g. C. P. $K_2Cr_2O_7$ was dissolved in one liter of solution. Calculate its molarity and its iron value.

9. The tin from 0.2800 g. of a sample of block tin, when in hydrochloric acid solution and in the stannous condition, was titrated with 0.0997 M $FeCl_3$ solution, 46.54 ml. being required. Calculate the percentage of tin in the sample.   Ans.   98.35%.

10. To 60.0 ml. of a stannous chloride solution an excess of approx. 0.1 M $FeCl_3$ solution was added, and the resultant solution then titrated with 0.1600 M $K_2Cr_2O_7$ solution, 40.0 ml. of the latter being required. How much $SnCl_2$ per milliliter did the original solution contain?
                              Ans.   0.0608 g. $SnCl_2$ per milliliter.

11. For the titration of ferrous ion, how many grams of potassium dichromate per liter of solution will give a solution equivalent to a solution of potassium permanganate containing 2.500 g. per liter?   Ans.   3.878 g.

12. In standardizing an approximately 0.03 M $KMnO_4$ solution by means of sodium oxalate, the following results were obtained:

Grams $Na_2C_2O_4$	ml. $KMnO_4$ solution used
0.3039	30.30
.3223	32.10
.3414	34.05

What was the average deviation?   What was the molarity of the $KMnO_4$ solution, and what was its value in terms of iron?
                Ans.   Av. dev.   = 0.5 part per 1,000.
                       Molarity   = 0.02996.
                       1 ml. $KMnO_4$ ≡ 0.008364 g. Fe.

13. The calcium oxalate precipitate from 1.1450 g. of a sample of rock was dissolved in dilute sulfuric acid and titrated with 0.01995 M $KMnO_4$, requiring 11.30 ml.   Find the percentage of CaO in the rock.
                                             Ans.   2.76%.

14. 100 ml. of a sample of commercial hydrogen peroxide solution were diluted to 1,000 ml., and 10 ml. of this diluted solution were titrated with titanous chloride solution (1 ml. of which ≡ 0.005156 g. Fe), the titration requiring 23.1 ml.   How many g. of H_2O_2 were present per 100 ml. of original H_2O_2 solution?   For method, see Knecht & Hibbert, *Ber.* **38**, 3324 (1905).   Ans.   3.63 g. H_2O_2 per 100 ml.

15. 1.000 g. of a sample of chrome-iron ore $FeO \cdot Cr_2O_3$ was oxidized by sodium peroxide, and one-fifth of the resulting chromate was treated with 35.24 ml. of a ferrous ammonium sulfate solution, which proved to be in slight excess.   The excess of ferrous ion was titrated back with 2.72 ml. of a potassium dichromate solution.   The values of the solutions were as follows: 1 ml. $Fe(NH_4)_2(SO_4)_2$ solution ≡ 0.005823 g. Fe; 1 ml. $K_2Cr_2O_7$ solution ≡ 0.006257 g. Fe.   Find the percentage of chromium in the ore.
                                             Ans.   29.20%.

16. The phosphorus in 5.000 g. of a sample of iron ore was precipitated as ammonium phospho-molybdate.   The precipitate was dissolved, etc., and the solution passed through a Jones reductor.   It then required 22.68 ml. $KMnO_4$ solution (1 ml. ≡ 0.005988 g. Fe) for the titration.

Find the percentage of phosphorus. Note: After passing through the reductor the molybdenum is in the form of Mo^{+++}; the permanganate oxidizes this to MoO_4^-.   Ans. 0.042%.

17. Given a solution of $KMnO_4$, 1 ml. $\equiv$ 0.008637 g. of $Na_2C_2O_4$. What weight of iron ore must be taken so that each milliliter of $KMnO_4$ solution used in titration shall correspond to 2% of iron in the ore?
                                                     Ans. 0.3600 g.

18. 25.06 ml. of $KMnO_4$ were required to titrate 0.2500 g. sodium oxalate. 30.00 ml. of the same solution were required to titrate a 2.0040 g. sample containing iron which also contained, on the moisture free basis, 5.10% of titanium. The sample contained 4.00% moisture. The Jones reductor method was used.
    (a) Calculate the iron value of the permanganate solution.
    (b) Calculate the titanium value of the permanganate solution.
    (c) Calculate the per cent of iron in the ore on the moisture free basis.

19. How many g. of $K_2Cr_2O_7$ per liter of solution will be required in order that 1 ml. of solution shall correspond to 1% of iron when 0.500 g. of iron ore is taken for analysis?   Ans. 4.391 g.

20. 30.12 ml. of 0.02042 M $KMnO_4$ was required to titrate a 0.8047 g. sample containing, on the dry basis, 2.12% of titanium and 3.66% of vanadium. The sample contained 3.22% moisture. Reduction was carried out by means of sulfide ion. Calculate the per cent of Fe on the dry basis.

21. 30.21 ml. of ceric sulfate solution were required to titrate 0.1697 g. of arsenous oxide. Calculate the molarity and the iron value of the ceric sulfate solution.

22. 37.21 ml. of 0.1175 M ceric sulfate solution were required to titrate the iron in a sample of ore. Calculate the weight of iron in the sample.

23. 31.64 ml. of 0.01521 M potassium dichromate solution were required to titrate the iron in a sample of ore. Calculate the weight of iron in the sample.

CHAPTER XVII

DETERMINATION OF MANGANESE OXIDIMETRICALLY AND GRAVIMETRICALLY

360. Methods of Separation. — Because of the fact that the great majority of the determinations of manganese are concerned with its presence either in manganese ores, manganese alloys, or in iron and steel products, and that these materials contain constituents the presence of which is incompatible with the use of certain of the methods of determination given below, there are several important separations which have to be accomplished time and again. Before discussing the methods for the determination of manganese, it will be convenient to describe the four most important methods of separation.

361. *The Zinc Oxide Method*.[1] *Separation of Ti^{++++}, Fe^{+++}, Al^{+++}, Cr^{+++}, $PO_4^{\equiv}$ from Ni^{++}, Co^{++}, Mn^{++}, Ca^{++}, Mg^{++}.* The zinc oxide method of separation is based on the fact that the concentration of hydroxyl ion in equilibrium with zinc oxide, which has been made into a creamy pulp with water, is sufficient to cause the precipitation of the hydroxides and phosphates of Ti^{++++}, Fe^{+++}, Al^{+++}, and Cr^{+++} but not sufficient to effect a similar precipitation with respect to Ni^{++}, Co^{++}, Mn^{++}, Ca^{++}, and Mg^{++}. The solution from which the above precipitation has been made, however, must not be allowed to stand any length of time before being used, because the manganous ion will slowly oxidize to manganic ion and the latter will precipitate out as $MnO \cdot OH$. This method can be used to advantage in conjunction with the Volhard method for determining manganese. The procedure is very simple: The solution containing the metals as sulfates is first neutralized with sodium carbonate to a pH of about 4.5 (neutral to methyl orange, or until there is formed a slight precipitate which dissolves very slowly when the solution is stirred briskly). The zinc oxide, previously made into a creamy pulp

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[1] P. Slawik, *Chem.-Ztg.*, **34**, 648 (1910).

with water in an agate mortar is added in small portions with vigorous stirring until it is present in small but unmistakable excess. The solution is then made up to definite volume (usually 1,000 ml.), and after being thoroughly shaken, is allowed to stand at room temperature for 30 minutes or so to allow the precipitation to complete itself and to allow the excess of zinc oxide to settle to the bottom of the flask. An aliquot portion (50–100 ml.) of the clear solution is then withdrawn by means of a pipette, and the manganese is determined by the Volhard method as described in §§ 367 and 368.

362. The Basic Acetate Method of Separating Ti^{++++}, Zr^{++++}, Fe^{+++}, Al^{+++}, Th^{+++}, Cr^{+++}, (partially) $PO_4^{\equiv}$ from Ni^{++} (partially) Co^{++} (partially) Zn^{++}, Mn^{++}, Ca^{++}, Mg^{++}, Ba^{++}.[2]— The basic acetate method of separation is an old and important method which is founded on the more pronounced hydrolysis of the salts of Ti^{++++}, Fe^{+++}, Al^{+++} in a solution faintly acid with acetic acid as compared with the salts of Ni^{++}, Co^{++}, Zn^{++}, Mn^{++}, Mg^{++}, and Ca^{++}. By the establishment of certain conditions described subsequently in §§ 367 and 368, the hydrolysis can be made to proceed to a point where the Ti^{++++}, Fe^{+++}, and Al^{+++} are quantitatively thrown out in the form of colloidal gels of the general composition $[Fe(CH_3COO)_3]_p[Fe(OH)_3]_q[H_2O]_r$ in which the ratio of $p : q : r$ is variable, whereas Ni^{++} and Co^{++} will be only partially thrown out, while Zn^{++}, Mn^{++}, Ca^{++}, and Mg^{++} will be thrown out to such a very small extent that a repetition of the process serves to keep them out of the iron and aluminum precipitate entirely. With respect to Cr^{+++}, it is to be mentioned that while salts of chromium undergo pronounced hydrolysis, the behavior of this element in the basic acetate separation is a matter of dispute, some workers claiming that practically all the chromium can be precipitated with the iron and aluminum, others claiming that the separation is not at all satisfactory when chromium is present.[3] Phosphorus in the usual form of phosphate ion $PO_4^{\equiv}$ will be quantitatively precipitated as ferric or aluminum phosphate, provided the iron and aluminum are in excess.

[2] Members of the copper and tin groups must first be removed by hydrogen sulfide as described in § 258.

[3] See Mellor, pp. 362, 469 of reference given in § 11.

Theory. — When the salt of a weak base and a strong acid is dissolved in water, it undergoes hydrolysis. In the case of ferric chloride, this hydrolysis may be represented by the equation

$$Fe^{+++} + 3\ H_2O \rightleftarrows Fe(OH)_3 + 3\ H^+.$$
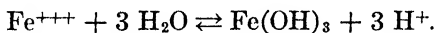
The ferric hydroxide which is formed does not precipitate out, but enters into combination with some of the ferric chloride that is left to form the ferric hydroxide sol, which [4] is probably a colloidal aggregate of the composition $[pFeCl_3 \cdot qFe(OH)_3 \cdot rH_2O]$, where the ratio of $p : q : r$ varies with conditions. It has been further shown that when the ratio of $FeCl_3 : Fe(OH)_3$ in the sol, namely, the ratio of $p : q$, becomes less than $1 : 20$, the sol becomes unstable and precipitates out as the gel $[pFeCl_3 \cdot qFe(OH)_3 \cdot rH_2O]$.

Hence, any agency which will decrease the ratio of $FeCl_3 : Fe(OH)_3$ beyond the limit $1 : 20$ will cause precipitation. By reference to the equilibrium scheme just given, it will be seen that, if we diminish the concentration of hydrogen ion, we promote the forward reaction and so cut down the concentration of Fe^{+++} and at the same time build up the concentration of $Fe(OH)_3$. Now there are two ways by which we can diminish the concentration of hydrogen ion:

1. By neutralization with hydroxyl ion by adding an alkali or alkaline salt.

2. By tying up the hydrogen ion in the form of a weak acid by the addition of a buffer salt. Both of these devices are made use of in the basic acetate separation. The solution containing the metals, preferably as chlorides, is carefully treated with a $2\ M$ solution of sodium carbonate until the concentration of hydrogen ion is diminished to a point where a very slight permanent precipitate is formed; the precipitate is then dissolved by the addition of a few drops of $3\ M$ hydrochloric acid; enough sodium acetate solution is then added to furnish a concentration of sodium acetate equal to $0.01\ M$ when the solution is subsequently diluted. The final dilution should be 100 ml. of solution for each 0.1 g. of iron (or aluminum) which is present.

In order further to decrease the ratio of $FeCl_3 : Fe(OH)_3$ and to bring about the precipitation of the gel $[pFeCl_3 \cdot qFe(OH)_3 \cdot rH_2O]$,

[4] A. W. Thomas and A. Frieden, *J. Am. Chem. Soc.*, **40**, 2522 (1923).

advantage is taken of the facts that increase of volume and increase of temperature both work toward this end. The solution containing the metals, after the addition of the requisite amount of sodium acetate, is diluted to the necessary volume with hot water, the solution is brought to boiling as quickly as possible, and is boiled for just 3 minutes. If the boiling is continued for too long a time, the precipitates tend to become slimy (probably due to dehydration of the gels) and difficult to filter. After the precipitation is complete, the solution (filtrate) should be neutral to methyl orange and slightly acid to methyl red. When the Ti^{++++}, Fe^{+++}, and Al^{+++} are in excess with respect to the $PO_4^{\equiv}$, as already stated, the Ti^{++++}, Fe^{+++}, Al^{+++}, and $PO_4^{\equiv}$, will be quantitatively precipitated, the Ni^{++} and Co^{++} partially precipitated, and the Zn^{++}, Mn^{++}, Mg^{++}, Ca^{++}, and Ba^{++} precipitated to a very slight extent. A repetition of the process serves to keep these last named elements out of the iron and aluminum precipitate entirely. If Ni^{++} and Co^{++} are present, it is best to separate them from the iron and aluminum precipitate after a second acetate separation has been made. This separation can be made by dissolving the precipitate of the second precipitation in dilute hydrochloric acid, adding excess of sodium acetate, and passing in hydrogen sulfide to precipitate the sulfides of nickel and cobalt.

363. The Bromine Method of Separating Mn^{++} from Zn^{++} (partially) Ca^{++}, Mg^{++}, Na^+, SO_4^- and $C_2H_3O_2^-$. — If Ni^{++} and Co^{++} are present, they must first be removed by hydrogen-sulfide precipitation from a solution faintly acid with acetic acid; otherwise they will also be oxidized and will precipitate out as higher oxides along with the manganese dioxide. The precipitation with hydrogen sulfide will also remove zinc.

Manganous ion can be oxidized to acid manganite ion and quantitatively precipitated as the hydrated manganese dioxide by means of bromine, provided the concentration of hydrogen ion of the solution lies between a pH of 4.0 and 7.0. If the solution is more acid than a pH of 4.0, the precipitation of the manganese will be incomplete because the potential demanded by such concentrations of hydrogen ion, that is 1.21–1.42 volts,[5] is greater

[5] See § 321.

than the bromine can furnish. If the solution is more alkaline than a pII of 7.0, say between a pH of 7.0 and 9.0, the potential required is much less than 1.21 volts and the bromine can effect the oxidation of the manganous ion, but care must be exercised in this region because the only practical way of our obtaining concentrations of hydrogen ion between a pII of 7 0 and 9.0 is by means of ammonium hydroxide buffered by an ammonium salt. Under such conditions, the ammonium ion of the solution is oxidized by the bromine according to the reaction

$$3 \text{ Br}_2 + 2 \text{ NH}_4^+ + 8 \text{ OII}^- \rightarrow \text{N}_2 + 8 \text{ II}_2\text{O} + 6 \text{ Br}^-.$$
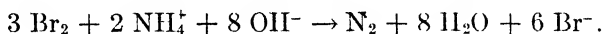
If the concentration of ammonium ion is too great, the potential at which this reaction takes place may be less than that required for the oxidation of the manganous ion, and so the precipitation of the manganese may be incomplete. If, therefore, ammonium hydroxide is used in conjunction with bromine, only a slight excess of ammonium hydroxide and ammonium salts should be present, and it is generally necessary to repeat the treatment with bromine to insure quantitative precipitation of the manganese.

If the solution is more alkaline than a pII of 9.0, the potential required for the oxidation of the manganous ion is still less than when the pII is between 7.0 and 9.0, but the concentration of hydroxyl ion now enters as an interfering factor because it is sufficient to cause the precipitation, not only of manganous hydroxide, but of zinc hydroxide as well. The best region in which to work is between a pH of 4.0 and 6.0. This concentration of hydrogen ion is readily established by having the solution faintly acid with acetic acid and buffered, if necessary, with sodium acetate. A concentration of the latter of 0.1 M is generally suitable.

The procedure is to add a small quantity of liquid bromine (1–2 ml.) to the faintly acid solution and to heat it to boiling to expel excess of bromine. The solution is filtered, and to the filtrate is added a little sodium carbonate until the filtrate is neutral to litmus, then a few drops of liquid bromine, after which the solution is heated to boiling as before and the excess of bromine is expelled. This second operation is for the purpose of insuring the quantitative precipitation of the manganese. The precipitated manganese dioxide is washed with hot water and is then dissolved

in a small quantity of 6 M hydrochloric acid to which a few milliliters of sulfurous acid (or sodium sulfite solution) have been added. This solution should be used for a reprecipitation of the manganese if much zinc, calcium, or magnesium was originally present, and if it is planned to determine the manganese gravimetrically by precipitation as manganese ammonium phosphate.

364. *The Chlorate Method of Separating* Mn^{++} *from* Fe^{+++} *(partially),* Al^{+++}, Ni^{++}, Co^{++}, Zn^{++}, Ca^{++}, Mg^{++} *in Strong Nitric Acid Solution.* — In the chlorate method of separation, the manganese is thrown out as manganese dioxide through the combined oxidizing agencies of the chlorate and nitrate ions in the presence of a high concentration of hydrogen ion. The principle and details of this separation are exactly the same as those which are employed in the Ford-Williams method for determining manganese and will be discussed in § 371. It should be noted that some iron will be dragged down with the manganese dioxide.

365. The Gibbs' Method for the Gravimetric Determination of Manganese.[6] — In the Gibbs' method, manganous ion is precipitated as manganese ammonium phosphate $MnNH_4PO_4 \cdot H_2O$ and ignited to manganese pyrophosphate $Mn_2P_2O_7$. Practically all ions but those of the alkalies must be absent. The method is suitable for amounts of manganese ranging from 2–200 mg. Mn, and is one of the best of all methods that we have for manganese.[7] The details of this method are given in the following paragraph.

366. Exercise No. 41. Determination of Manganese in Spiegel; Gibbs' Gravimetric Method. — Spiegel is an alloy of manganese and iron containing about 17–20% of manganese. Weigh accu-

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[6] W. Gibbs, *Chem. News*, **17**, 195 (1868); *Am. J. Sci.* (2) **44**, 216 (1867); *Z. anal. Chem.*, **7**, 101 (1868).

[7] It might be thought that the precipitate of manganese dioxide, which can be obtained readily enough through the oxidation of manganous ion, either in acid or alkaline solution, could be used as the basis of a gravimetric method for manganese, but such is not the case because the manganese dioxide is of variable composition and cannot be dried or ignited so as to furnish a compound of definite composition. Strong ignition of manganese dioxide with access of air at the full heat of the Meker burner gives results which show but a poor approximation to Mn_3O_4 as the composition of the ignited product.

rately about 1 g. of the sample of this alloy and transfer it to a casserole. Cover with a watch-glass and treat with about 20 ml. of 8 M nitric acid. Evaporate to dryness and heat strongly to destroy organic matter. Cool and add 20 ml. of 3 M hydrochloric acid and evaporate to dryness again in order to remove the nitric acid. Moisten the residue with 12 M hydrochloric acid and add 40–50 ml. of boiling water to dissolve the soluble salts. Filter off the silica, and to the cold filtrate (which should have a volume of about 100 ml.) add a solution of 2 M sodium carbonate until the precipitate which is formed dissolves very slowly; then add the sodium carbonate solution, dropwise, until a very slight permanent precipitate is formed. Redissolve the precipitate by the addition of a few drops of 3 M hydrochloric acid. Transfer the clear deep-red solution to a liter beaker, dilute to about 400 ml. with cold water, add 7 ml. of 1 M sodium acetate solution, then add 300 ml. of boiling water and heat the solution to boiling as quickly as possible, and continue the boiling for just 3 minutes. Filter the hot solution at once through a large fluted filter paper and wash the precipitate a few times with 0.1 M sodium acetate solution. Dissolve the precipitate in as little hot 3 M hydrochloric acid as possible, and repeat the basic acetate precipitation, washing the precipitate thoroughly with hot 0.1 M sodium acetate solution. Add this filtrate to the first filtrate and concentrate the combined filtrates to about 250 ml. If during this evaporation a small precipitate separates out of the solution, it must be removed by filtration. This precipitate is then dissolved in a small amount of 3 M hydrochloric acid and another basic acetate separation is made in a solution the total volume of which is not over 50 ml. Filter and add the filtrate to the main portion. Transfer the combined filtrates to a large Erlenmeyer flask, add about 15 ml. of 2 M sodium acetate solution, heat to 90°–95°, and then saturate with hydrogen sulfide under pressure.[8] Digest until any precipitate coagulates and settles, filter while hot, and wash the precipitate with water saturated with hydrogen sulfide.

The next step is the precipitation of the manganese as manganese dioxide by means of bromine. This operation might seem

[8] The saturation with hydrogen sulfide may be omitted if it is known that nickel and cobalt are absent.

unnecessary in the case of a spiegel since the latter contains no zinc, magnesium, or calcium to give insoluble phosphates, but there is such an accumulation of sodium salts at this juncture that a reprecipitation of the manganous ammonium phosphate would be necessary; hence it is a better plan to throw out the manganese at this point as the dioxide. Boil out the hydrogen sulfide from the filtrate, allow the latter to cool, and add 2–3 ml. of bromine (not bromine water); heat to expel the excess of bromine and filter. To the filtrate add a few drops more of bromine and a few drops of 2 M sodium carbonate solution in order to make the filtrate slightly more alkaline so as to insure the complete precipitation of the manganese. If more manganese dioxide is obtained, filter and wash it, and add it to the main portion. Dissolve the manganese dioxide from the filter with hot 3 M hydrochloric acid containing a little sulfurous acid.

Dilute the solution to about 150 ml. and add a solution of di-ammonium hydrogen phosphate $(NH_4)_2HPO_4$ in considerable excess, namely, about five times the theoretical amount necessary to combine with the manganese.[9] If a precipitate should form at this point, dissolve it by the cautious addition of 3 M hydrochloric acid. Now heat the solution to 90°–95° on the water-bath and add 3 M ammonium hydroxide, dropwise and with constant stirring, until a flocculent precipitate begins to form; this precipitate is $Mn_3(PO_4)_2$. Continue the heating until the precipitate becomes changed over into the crystalline $MnNH_4\cdot PO_4\cdot H_2O$; then add another drop of ammonium hydroxide, and so on until further additions cause no appreciable change. Care must be taken, however, that in the end there shall be only a very slight excess of ammonium hydroxide. The precipitate of $MnNH_4\cdot PO_4\cdot H_2O$ is nearly white with a characteristic nacreous luster and is one of the easiest precipitates known to filter and wash. If an excess of ammonium hydroxide has been added, the precipitate may be brown in color, in which case add 3 M hydrochloric acid until the precipitate dissolves and repeat the precipitation as

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[9] 1 ml. 0.1 M $(NH_4)_2HPO_4 \equiv$ 5.5 mg. Mn. The di-ammonium hydrogen phosphate solution may be readily prepared by neutralizing phosphoric acid with ammonium hydroxide until the solution just turns pink when phenolphthalein is used as the indicator.

described above.   As soon as the precipitate has become crystalline in character, allow the solution to cool to room temperature and then filter through a Gooch crucible and wash with 0.1 M ammonium nitrate solution until the washings give no test for chloride ion.   Dry the precipitate at $100°$–$105°$ and weigh as $MnNH_4PO_4 \cdot H_2O$, or ignite it at the full heat of the Meker burner and weigh as $Mn_2P_2O_7$.

367. Volhard's Method for the Oxidimetric Determination of Manganese.[10] — In the Volhard method, the manganese which is to be determined is separated from other substances and brought into the form of manganous sulfate, the titration then being effected by oxidizing the manganous ion to the acid manganite ion by means of permanganate ion, the latter itself being reduced only to the acid manganite ion.   This reaction may be represented as follows,

$$2\ MnO_4^- + 3\ Mn^{++} + 7\ H_2O \to 5\ HMnO_3^- + 9H^+.$$

Owing to the fact that acid manganite ion $HMnO_3^-$ forms an insoluble precipitate with manganous ion, according to the reaction,
$$2\ HMnO_3^- + Mn^{++} \to Mn\ (HMnO_3)_2 \downarrow,$$
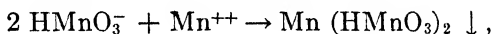
some of the manganous ion which is being titrated will be removed in the form of the insoluble manganous acid manganite (manganese dioxide) without being oxidized.   The titration of a given weight of manganous ion will, therefore, require less permanganate than corresponds to that calculated from the changes of charge involved. It might be thought that the error thus introduced into the determination could be compensated for by running a control (§ 56), but, unfortunately, the weight of manganous ion that is removed as manganous acid manganite varies from one duplicate determination to another.   To get around this difficulty, Volhard added to the solution of manganous sulfate a relatively high concentration of zinc sulfate (§ 368).   The zinc ion reacts with the acid manganite ion in a manner analogous to the manganous ion as shown in the following equation,

$$2\ HMnO_3^- + Zn^{++} \to Zn(HMnO_3)_2 \downarrow.$$
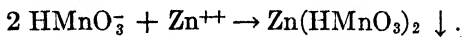
[10] A. Guyard, *Chem. News*, **8**, 292 (1863); *Z. anal. Chem.*, **3**, 373 (1864); J. Volhard, *Liebigs Ann. Chem.*, **198**, 218 (1879); *Chem. News*, **40**, 207 (1879).

Because of the smaller solubility product of zinc acid manganite, the precipitation of the latter takes place almost to the entire exclusion of the precipitation of manganous acid manganite, thereby permitting the titration of the manganous ion with tolerable precision, particularly if a control is run in the presence of zinc sulfate (§ 372, Example 1). Results obtained by Volhard's method without the presence of the zinc ion are absolutely unreliable. The solution being titrated should be free from chloride, nitrate and all cations except manganous ion, zinc ion and hydrogen ion. The solution should be faintly acid with sulfuric acid and should be maintained at about 95° during titration. The standard permanganate solution should be added dropwise until the characteristic permanganate end point is reached.

Precision. — This method can be used for amounts of manganese ranging from 10–80 mg. of Mn. The average deviation of the method for amounts over 40 mg. of Mn is about 2 parts per 1,000; the constant error is about 12 parts per 1,000, the method giving low results (see § 372, Example 1, in this regard). The details of this method are given in the following paragraph.

368. Exercise No. 42.   Oxidimetric Determination of Manganese in a Manganese Ore.   Volhard Method. — The chief ores of manganese are pyrolusite MnO_2 and braunite $3 Mn_2O_3 \cdot MnSiO_3$, with typical analyses as follows:

	Pyrolusite [11]	Braunite [12]
MnO_2	94.0%	44.0%
MnO	2.41	45.57
Fe_2O_3	.49	. . . . .
CaO	.25	.91
SiO_2	.55	8.63
H_2O	2.33	. . . . .

Procedure. — Treat about 1 g. of the ore, previously ground to a fineness of 100 mesh or so, in a covered casserole with 20 ml. of

[11] Dana, p. 244 of reference given in § 1.
[12] *Ibid.*, p. 233.

12 M hydrochloric acid. Heat gently until decomposition is effected (if sulfides are present, add about 5 ml. of 18 M nitric acid toward the end of the process), and then add 25 ml. of water and 5 ml. of 18 M sulfuric acid and evaporate until fumes of sulfur trioxide are copiously evolved. Cool, add about 150 ml. of water and heat until all soluble salts are dissolved. If the insoluble residue indicates incomplete decomposition of the ore, filter and fuse the residue with sodium carbonate; allow the fused mass to cool, and then dissolve it in hydrochloric acid. Add a few milliliters of sulfuric acid, and evaporate to fumes of SO_3 as before. Allow to cool, dilute with a few milliliters of water, and add the solution thus obtained to the main solution.

To the combined solutions add a 2 M solution of sodium carbonate until the pH of the solution is about 4.5 (neutral to methyl orange) or until there is formed a slight precipitate which dissolves very slowly when the solution is stirred; then transfer the solution to a graduated liter flask. Add a suspension of zinc oxide in water, a little at a time and with thorough stirring after each addition, until all the iron, aluminum, etc., have been precipitated and the zinc oxide is in slight excess; then make up to the mark and mix the solution thoroughly by shaking. Because of the volume occupied by the precipitated hydroxides and the excess of zinc oxide, it is advisable to make the solution up to as large a volume as practicable, say, 1,000 ml., as by this procedure the error which is introduced by the solids occupying space is greatly reduced. For a similar reason, the excess of zinc oxide should be kept as small as possible. Either allow the solution to settle and remove aliquot portions of the clear supernatant solution by means of a pipette, or filter through a dry filter, discarding the first 25 ml. or so of the filtrate. For the titration, 200 ml. portions of the clear solution should be employed, and these portions should be measured accurately by means of a pipette or graduated flask.[13] Place a 200 ml. portion in a casserole, add 25 ml. of 2 M zinc sulfate, then 1–2 drops of methyl-orange solution and enough 0.05 M

[13] If the analysis must be interrupted at this juncture, measure out three portions and acidulate with 0.05 M sulfuric acid until slightly acid to methyl orange; otherwise $MnO.OH$ will gradually precipitate out as the solution stands.

sulfuric acid to make the solution faintly acid to the methyl orange, then heat to boiling. Add from a burette, one milliliter at a time, standard permanganate solution and stir vigorously after each addition. Continue the titration until the solution which is being titrated shows a faint pink color against the wall of the white casserole. If it should happen during the titration (as it often does), that a finely divided deposit of zinc acid manganite collects on the wall of the casserole and practically obscures the end point, transfer the solution to a fresh casserole as the end point is approached, heat to near boiling, and finish the titration by adding the permanganate solution, drop by drop, until an end point is established which lasts for at least 60 seconds. If it is impossible to establish an end point of this permanency, some foreign reducing agent is present, probably chloride ion, and the determination should, accordingly, be rejected.

Duplicate determinations should agree to within 2 parts per 1,000, upon the assumption that 25 ml. or more of standard permanganate solution has been used in the titration. The calculation of results is made after the manner shown in § 372, Example 1.

369. The Sodium Bismuthate Method of Determining Manganese.[14]—Manganese ion is oxidized to permanganate ion by means of sodium bismuthate in the presence of nitric acid. The excess of sodium bismuthate is filtered off, and the permanganate ion is reduced by means of an excess of standard ferrous sulfate solution, the amount of excess being determined by back titration with standard potassium permanganate solution; in an alternative method the permanganate ion may be titrated directly to an end point by means of sodium arsenite solution. Iron does not interfere but chromium and vanadium do, unless sodium arsenite is used as the reducing agent. The alternative method should be used only for amounts of manganese ranging from 2 to 20 mg. of Mn. It is particularly applicable for the determination of manganese in iron and steel products and manganese alloys. The details of this method are given in § 443, where it is applied to the determination of manganese in a tungsten steel.

[14] Schneider, *Dinglers Polytech. J.*, **269**, 224 (1888); Reddrop and Ramage, *Trans. Chem. Soc.*, **67**, 268 (1895).

370. The Persulfate Method of Determining Manganese.[15]—
In the persulfate method manganous ion is oxidized to permanganate ion in sulfuric acid solution by means of persulfate ion in the presence of silver ion as a catalyst. The permanganate ion, after removal of the silver ion as silver chloride, is titrated with sodium arsenite solution. Excess of persulfate ion does not interfere, as there is practically no reduction of persulfate ion by arsenite ion. Chromium and vanadium do not interfere. The method can be used only for amounts of manganese ranging from 2 to 10 mg. Mn. It is not very generally used because for some unknown reason the oxidizing behavior of persulfate ion is sometimes very erratic. For further details, see Boyle, *Ind. Eng. Chem.*, **4**, 202 (1912).

371. The Ford-Williams Method of Determining Manganese.[16]
In the Ford-Williams method, manganous ion in a solution free from chloride and sulfate is oxidized to the acid manganite ion (manganese dioxide) by heating with chlorate ion in the presence of concentrated nitric acid at a temperature of 95°–100°. Care must be taken to add to the solution the salt which furnishes the chlorate ion *only when the solution is cool* (not over 60°), as serious explosions will result if the salt ($NaClO_3$) is added to the boiling solution. After the salt has been added, the solution may be heated.

The manganese dioxide which precipitates will always drag down some iron if this latter element is present. The precipitate of manganese dioxide is filtered off on asbestos and washed with water until the washings give no test for acid when tested with litmus paper. The precipitate and asbestos are placed in the flask in which the precipitation was effected, and a known amount of standard ferrous sulfate solution is added. An excess of ferrous sulfate solution must be used. The flask is shaken until the manganese dioxide is completely dissolved, after which the excess of ferrous ion is titrated by means of standard permanganate solution. This method is useful for amounts of manganese

[15] G. v. Knorre, *Z. angew. Chem.*, **14**, 1149 (1901).

[16] A. P. Ford, *Trans Am. Inst. Min. Eng.*, **9**, 397 (1880); F. Williams, *ibid.*, **10**, 100 (1881); W. Hampe and M. Ukema, *Z. anal. Chem.*, **24**, 431 (1885); *ibid.* **32**, 369 (1893).

ranging from 2 to 20 mg. of Mn.   It can be employed to advantage in the determination of small amounts of manganese in the presence of large quantities of iron in pig iron, etc.   As the precipitate has not the exact composition MnO_2 but is slightly deficient in oxygen, a blank determination should be run on a standard steel of known manganese content.

372. Examples.

1. In determining the percentage of manganese in an ore by Volhard's method, a standard solution of potassium permanganate (1 ml. $\equiv$ 0.010033 g. $Na_2C_2O_4$) was used as a source to supply a known weight of manganous ion, the manganous ion then being oxidized to acid manganite ion (manganese dioxide) by means of the same standard permanganate solution.   The procedure was as follows: known weights of sodium oxalate were dissolved in 50 ml. of water and 2 ml. of 9 M sulfuric acid added; the solution was heated to 90° and titrated with the permanganate solution.   The results were:

	a	b	c
Grams $Na_2C_2O_4$	0.4020	0.4005	0.4015
ml. $KMnO_4$ solution	40.15	40.10	40.10

After titration each of the solutions was neutralized to methyl orange with 2 M sodium carbonate, 25 ml. 2 M zinc sulfate solution were added and the solution heated to 90°–95°; the permanganate solution was then added until the end point was reached.   The results were:

	a	b	c
ml. $KMnO_4$ solution	26.40	26.40	26.40

How many grams of manganese does 1 ml. of the permanganate solution oxidize?   What was the average deviation?   How many grams of manganese should 1 ml. of the permanganate solution oxidize theoretically? What is the constant error?

> Ans.   0.002498 g. Mn.;   1.2 parts per 1000.
> 0.002469 g. Mn.; 11.6 parts per 1000.

2. The standard permanganate solution of Example 1 was used in the determination of manganese in an ore by Volhard's method.   1.002 g. sample was taken, dissolved, etc., and the solution was made up to 1000 ml. Aliquot portions of 200 ml. were taken, the pH was adjusted, 25 ml. of 2 M zinc sulfate solution was added to each, and the portions were heated to 90°–95° and titrated with the permanganate solution.   The results were:

	a	b	c	d
ml. $KMnO_4$ required	47.10	47.02	47.30	47.28

What was the percentage of manganese in the ore?   What was the average deviation?   Ans.   58.77%; 1.7 parts per 1000.

3. In determining the percentage of manganese in a spiegel by Volhard's method, 1.000 g. of sample was taken, dissolved, etc., and the solution made up to 1000 ml. Aliquot portions of 200 ml. were taken, the pH adjusted, 25 ml. 2 M $ZnSO_4$ added, etc., and titrated with a potassium permanganate solution, 1 ml. of which would oxidize 0.001655 g. Mn^{++} to MnO_2 by Volhard's method; 22.31 ml. were required. What was the percentage of manganese?   Ans. 18.46%

4. The manganese in a 1.1745 g. sample of manganese ore containing 1.16% moisture required 24.16 ml. of potassium permanganate solution when titrated by Volhard's method. One milliliter of the permanganate solution is equivalent to 0.01216 g. of sodium oxalate. Calculate the per cent of MnO_2 in the ore on the dry basis. Assume that all of the manganese in the ore is present as MnO_2.

5. In determining manganese in a sample of steel by the sodium bismuthate method 40.00 ml. of 0.04814 M ferrous sulfate solution was added.   The excess ferrous ion was then titrated with 20.16 ml. of 0.01149 M potassium permanganate solution. Calculate the weight of manganese in the sample.

6. When 45.00 ml. of ferrous ammonium sulfate solution was titrated in molar sulfuric acid solution 13.50 ml. of 0.02114 M permanganate solution was required. If the same ferrous ammonium sulfate solution is to be used in determining manganese in steel by the sodium bismuthate method, what weight of sample must be taken if 1.00 ml. of solution is to represent 0.1% of manganese in the sample?

CHAPTER XVIII

IODIMETRIC METHODS

373. General Consideration. — The reaction,

$$2\,I^- \rightarrow I_2 + 2\,e,$$
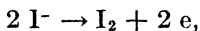
finds frequent application in analysis due, in part, to the fact that it can be quantitatively effected by such important oxidizing agents as permanganate, dichromate, hypochlorite, ferricyanide, arsenate, antimonate, and cupric ions and by hydrogen peroxide. By determining the amount of iodine produced by oxidation, the quantity of oxidizing agent involved can be calculated. The iodine can be determined by titrating with standard sodium thiosulfate solution. The reaction involved is,

$$I_2 + 2\,S_2O_3^= \rightarrow 2\,I^- + S_4O_6^=.$$
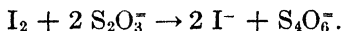
When only a small amount of the iodine remains unreduced, 2–3 ml. of a 1% starch solution is added. A pronounced blue color is produced, which disappears when the iodine has been quantitatively reduced to iodide ion.

The reverse reaction,

$$2\,e + I_2 \rightarrow 2\,I^-,$$
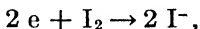
finds frequent application because it can be effected quantitatively by such important reducing agents as arsenite, stannous, sulfide, sulfite, and thiosulfate ions. In these cases, a standard iodine solution may be added to the reducing agent in the presence of starch solution until a blue color appears. This color is produced by the extremely small concentration of iodine which the solution acquires when the reducing agent has been quantitatively oxidized. An alternative method is to add the reducing agent to a measured amount of standard iodine solution which is known to be in excess and then to titrate the excess of iodine with standard sodium thiosulfate solution. The starch solution must not be added until just prior to the reaching of the stoichiometric point.

374. Starch Indicator. — The blue color which small concentrations of iodine give in the presence of small concentrations of starch solution was formerly thought to be due to the formation of an iodo-starch compound but is now believed to be due to the formation of a colloidal sol made of the soluble portion of the starch (β-amylose), iodide ion, and iodine, and having the general composition (β-amylose)$_p$(iodide ion)$_q$(iodine)$_r$(H$_2$O)$_s$ in which the values of q and r are small, relative to p. The important thing is that all four of these factors must be present for the development of the blue color; thus, if iodine is present but no iodide ion, there will be no blue color.[1]

Now starch yields, in addition to β-amylose (granulose), which is the soluble portion of starch and apparently a pure carbohydrate, another product called α-amylose (amylopectin or starch cellulose), which is insoluble. The α-amylose obtained from cereal seems to be a carbohydrate in combination with a fatty acid of the nature of oleic or linoleic acid. This α-amylose gives a reddish color with iodine, which is not discharged nearly as readily as the blue color of the β-amylose, and in this sense it is objectionable; fortunately, however, α-amylose constitutes only a small fraction of starch, say from 2 % in potato starch to 15 % in corn starch. Hence, by the simple choice of potato starch, the disturbing influence due to α-amylose is rendered negligible.

Starch, which has the empirical formula $(C_6H_{10}O_5)_n$, occurs in the cells of many plants in the form of circular or elongated microscopic granules. These granules are insoluble in water and it is only when heated up to 50° with water that they burst and yield the insoluble α-amylose and the soluble β-amylose. Both these products are quite rapidly hydrolyzed in aqueous solution into their degradation products — amylodextrin, erythrodextrin, achroodextrin, etc., if the concentration of hydrogen ion is greater than 10^{-2}. All these degradation products give, with iodine, red colors which are not discharged at the stoichiometric point. Hence, it is important that in iodine titrations, the starch solution should not be added until the stoichiometric point is just about to be

[1] Lottermoser, *Z. angew. Chem.*, **37**, 84 (1924); *Z. Elektrochem.*, **27**, 496 (1921).

reached. This is particularly apropos when the titration is being conducted in an acid solution, as is often the case.

We may sum up briefly the purport of the foregoing remarks into a few simple rules for the use of starch solution as an indicator in iodine titrations:

1. Make up fresh starch solution each day.

2. Do not add the starch solution to the solution being titrated until the end point is just about to be reached.

3. Always add the same amount of starch solution to each titration, that is, 2 or 3 ml. of a 1 % solution.

The starch solution is easily prepared by rubbing 2 g. of starch (preferably potato starch) into a thin paste with a little cold water and then pouring the paste into 200 ml. of boiling water. The insoluble portion (α-amylose) is allowed to settle, and the clear solution (β-amylose) above it is pipetted or decanted off for use. Starch solutions can be preserved by shaking with a small amount of toluene.

375. Sodium Thiosulfate Solution. — In practically all determinations involving iodine, the iodine is titrated by means of thiosulfate ion, according to the equation,

$$I_2 + 2\ S_2O_3^- \rightarrow 2\ I^- + S_4O_6^-$$
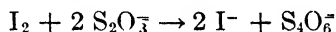
the thiosulfate ion being oxidized to the tetrathionate ion. This reaction takes place, as indicated, over a wide latitude of hydrogen ion concentration, from a pH of about 8.0 to a pH of about 0.5. If the solution, however, is more alkaline than a pH of 8.0, then less thiosulfate is required; if more acid than a pH of 0.5, more thiosulfate is required.[2] The salt that is used to supply the thiosulfate ion is sodium thiosulfate, which has the formula $Na_2S_2O_3 \cdot 5H_2O$. Although actual samples of the crystalline salt conform very closely to this formula, for accurate work it cannot be weighed out directly as a primary standard because of the variability in its water content. An approximate amount of salt must be weighed out and made up to volume and the resultant solution standardized. For such purposes, we can consider the composition of the crystalline salt as roughly $Na_2S_2O_3 \cdot 5\ H_2O$,

[2] See W. C. Vosburgh, *J. Am. Chem. Soc.*, **44**, 2120 (1922).

which means that 24.82 g. of the crystalline salt made up to one liter will give a solution which is approximately 0.1 M.

Thiosulfate ion slowly decomposes in aqueous solutions so that the value of a standard solution of sodium thiosulfate should be frequently redetermined. The change in value of the solution may result from a number of causes. In the first place, oxygen from the air may bring about the following reaction,

$$2\,S_2O_3^= + O_2 \rightarrow 2\,SO_4^= + 2\,S,$$
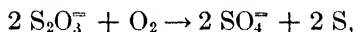
thereby lowering the iodine value of the solution. The presence in the solution of carbon dioxide from the air may produce sufficient acidity to cause the reaction,

$$S_2O_3^= + H^+ \rightarrow HSO_3^- + S.$$
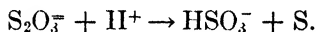
This change would have the effect of increasing the iodine value of the solution since the conversion of one HSO_3^- ion to sulfate ion liberates two electrons, whereas the conversion of one $S_2O_3^=$ ion to tetrathionate ion liberates only one electron. The action of bacteria which may be present in the water and exposure of the solution to light also may result in a change in the value of the thiosulfate solution.

376. Standardization of Sodium Thiosulfate Solution. — There are several ways of standardizing sodium thiosulfate solution. These methods include standardization by means of

1. Standard permanganate solution
2. Potassium dichromate
3. Potassium iodate
4. Resublimed iodine
5. Pure copper

We shall now describe the several methods in the above order.

377. *Standardization by Potassium Permanganate.*[3] — It is necessary to prepare enough 1.8 M potassium iodide solution for the work in hand[4] and run a blank on it to see that it is free from iodate.

The 1.8 M potassium iodide solution is prepared by dissolving

[3] Due to Volhard, *Liebigs Ann. Chem.*, **242**, 98 (1887).

[4] Wherever iodide ion is to function as a reducing agent in an analytical procedure, it is customary to use 10 ml. of 1.8 M potassium iodide solution (that is, 3 g. KI) to each determination.

15 g. of potassium iodide in a small quantity of water and making the volume up to 50 ml. The blank is run by adding 10 ml. of the potassium iodide solution to 400 ml. of water, 10 ml. of 9 M sulfuric acid, 3 ml. of a 1 % starch solution, and then titrating at once with approximately 0.1 M sodium thiosulfate solution. If the blank requires more than 0.20 ml. of 0.1 M $Na_2S_2O_3$, the potassium iodide should be rejected; if the blank requires less than 0.20 ml., the potassium iodide is satisfactory, but the blank which is obtained must be taken account of when calculating the value of the thiosulfate solution. Potassium iodide is always likely to contain small amounts of potassium iodate. As iodate ion acts as an oxidizing agent according to the equation,

$$6\,e + IO_3^- + 6\,H^+ \rightarrow I^- + 3\,H_2O,$$
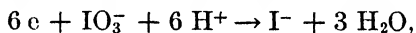
and thereby brings about the oxidation of thiosulfate ion, it is always necessary to run the blank on the potassium iodide under conditions parallel to those obtaining subsequently in the titration. With respect to the blank as well as to iodine titrations in general, it is to be noted that iodide ion is more or less rapidly oxidized to iodine by the dissolved oxygen in the solution, particularly at concentrations of hydrogen ion greater than 0.3 M, so that all iodine titrations should be made as quickly as possible after the iodine has been quantitatively liberated.

Assuming that a satisfactory blank has been obtained for the potassium iodide solution, the sodium thiosulfate solution is standardized by adding first 10 ml. of the 1.8 M potassium iodide solution to 400 ml. of water, then 10 ml. of 9 M sulfuric acid, and then by running in, with constant stirring, 25–30 ml. of approximately 0.02 M standard potassium permanganate solution, noting the exact amount added. The solution is titrated at once with the sodium thiosulfate solution until the color of the liberated iodine has nearly disappeared, after which 3 ml. of a 1% starch solution is added and the titration is continued to the disappearance of the blue color. *It is very important that the above order of adding the reagents is followed exactly.* Triplicate determinations are run and the result for each separate determination is calculated, taking care in each case to correct for the blank. The average deviation should not be greater than 1 part per 1,000.

The reactions involved in this determination are

$$2\,MnO_4^- + 10\,I^- + 16\,H^+ \rightarrow 2\,Mn^{++} + 5\,I_2 + 8\,H_2O$$

and

$$I_2 + 2\,S_2O_3^- \rightarrow 2\,I^- + S_4O_6^-.$$
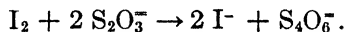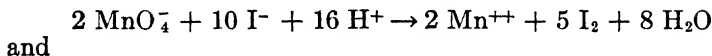
Since two thiosulfate ions are equivalent to one molecule of iodine, and five molecules of iodine are equivalent to two permanganate ions, it follows that

$$10\,S_2O_3^- \equiv 5\,I_2 \equiv 2\,MnO_4^-$$

and, therefore,

$$5\,Na_2S_2O_3 \equiv KMnO_4.$$
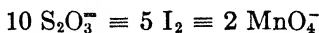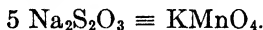
This relationship could have been arrived at by ignoring the part played by the iodine and considering only the partial equations,

$$5\,e + 8\,H^+ + MnO_4^- \rightarrow Mn^{++} + 4\,H_2O.$$

and

$$2\,S_2O_3^- \rightarrow S_4O_6^- + 2\,e.$$
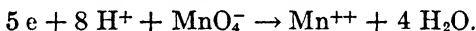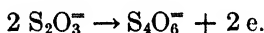
Multiplying these equations by 2 and 5, respectively, we find that

$$10\,S_2O_3^- \equiv 2\,MnO_4^-,$$
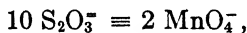
whence,
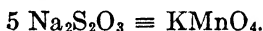
$$5\,Na_2S_2O_3 \equiv KMnO_4.$$

To illustrate the calculation of the molarity of a solution of sodium thiosulfate, let us suppose that 30.00 ml. of 0.02010 M $KMnO_4$ solution requires the addition of 40.30 ml. of the $Na_2S_2O_3$ solution. It follows from the stoichiometric relationship that, if the volumes of the two solutions had been equal, the molarity of the $Na_2S_2O_3$ solution would have been five times that of the $KMnO_4$ solution. Actually,

$$\frac{30.00}{40.30} = 0.7444 \text{ ml. } KMnO_4 \text{ solution} \equiv 1.0000 \text{ ml. } Na_2S_2O_3$$

solution. It follows that

$$0.02010 \times 5 \times 0.7444 = 0.07481 = \text{Molarity of } Na_2S_2O_3 \text{ solution.}$$

378. Standardization by Potassium Dichromate. — When potassium dichromate is used in standardizing sodium thiosulfate solution, it should be of a high grade of purity, being free of

chloride and sulfate. Technical or commercial grades of potassium dichromate are almost sure to contain chlorides or sulfates; by submitting them to three or four recrystallizations, however, it is possible to obtain a very pure product. The better grades of potassium dichromate which are supplied for analytical purposes usually conform to a very high degree of purity with the exception that the salt is likely to have retained a little water from its crystallization, even though subsequently dried by the manufacturer. To get rid of this moisture, it is best to heat the salt in a platinum crucible to a point just above its fusion point, which is 396°; drying at 100°–105° is entirely inefficacious.[5] Care must be taken to exclude all dust and organic matter. The fused salt, after it has cooled, may be crushed to a powder in an agate mortar; it should then be put in a glass-stoppered bottle to protect it from dust. A 0.01666 M solution of $K_2Cr_2O_7$ is prepared by dissolving 4.903 g. of pure and moisture-free salt in about 100 ml. of water and carefully making the solution up to one liter.

The procedure of standardization is very similar to that which is employed when potassium permanganate is used. First 50 ml. of 1.8 M potassium iodide solution is prepared and then a blank is run on it for the presence of iodate. The blank is determined by adding 10 ml. of the potassium iodide solution to 400 ml. of water, then 10 ml. of 12 M hydrochloric[6] acid is added and the solution is allowed to stand for 3 minutes out of direct sunlight. Then 3 ml. of a 1% starch solution is added and the solution is titrated at once with the approximately 0.1 M sodium thiosulfate solution. If the blank requires more than 0.20 ml. of 0.1 M $Na_2S_2O_3$, the potassium iodide should be rejected; if the blank requires 0.20 ml. or less, the potassium iodide is satisfactory but the blank must be taken account of when calculating the value of the thiosulfate solution.

Assuming a satisfactory blank, 10 ml. of the 1.8 M potassium iodide solution is added to 200 ml. of water followed by 5 ml. of

[5] Vosburgh, *J. Am. Chem. Soc.*, **44**, 2120 (1922) gives as his experience that it takes 9 hours of heating at 160° to drive off the moisture from the crystals of potassium dichromate.

[6] Hydrochloric acid is used later in the standardization when the dichromate ion is being reduced by iodide ion.

12 M hydrochloric acid. Then 25–30 ml. of the standard dichro-
mate solution is run in with constant stirring, noting the exact
amount added. The mixed solution is allowed to stand out of
direct sunlight for 3 minutes. It is then diluted to 400 ml. with
water and titrated with approximately 0.1 M sodium thiosulfate
solution until the brown color of the iodine becomes barely dis-
cernible, then 3 ml. of the starch solution is added and titration
is continued until the dark blue-green color changes to light green.
Triplicate determinations are run and the results are calculated
separately, taking care in each case to correct for the blank. The
average deviation should not be greater than 1 part per 1,000.
With respect to the constant error, it seems from the work of
Vosburgh [7] that this is within 1 part per 1,000.

In this method the partial equations involved in the calculation
of the molarity of the sodium thiosulfate solution are

$$6\ e + 14\ H^+ + Cr_2O_7^- \rightarrow 2\ Cr^{+++} + 7\ H_2O$$

and

$$2\ S_2O_3^- \rightarrow S_4O_6^- + 2\ e;$$

whence,

$$6\ Na_2S_2O_3 \equiv K_2Cr_2O_7.$$
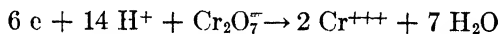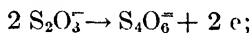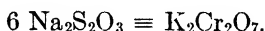
379. Standardization by Potassium Iodate. — Potassium iodate
which has been purified by recrystallization and drying may be
used as a standard for sodium thiosulfate solution. In the
presence of iodide ion in a slightly acid solution, iodate ion is
reduced to iodine and iodide ion is oxidized to iodine. The
iodine is then titrated with the sodium thiosulfate solution.

A solution of potassium iodate is prepared by carefully weighing
out between 1.30 and 1.50 g. of KIO_3, and dissolving in about
200 ml. of water and then diluting carefully to one liter.

To a 100 ml. portion of this solution measured by means of
an accurately calibrated 100 ml. pipette, 10 ml. of 1.8 M potassium
iodide solution and 3 ml. of 12 M hydrochloric acid are added. This
solution is titrated with the sodium thiosulfate until the solution
acquires a light yellow color, after which 3 ml. of a 1% starch
solution is added and the titration is continued until the blue color
of the solution has been completely removed.

[7] *J. Am. Chem. Soc.*, **44**, 2129 (1922).

The reactions involved in this method are

$$IO_3^- + 5\ I^- + 6\ H^+ \rightarrow 3\ I_2 + 3\ H_2O$$

$$I_2 + 2\ S_2O_3^- \rightarrow 2\ I^- + S_4O_6^-$$
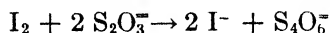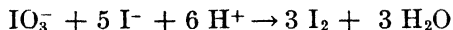
and, consequently, the relationship upon which calculations of molarity are based is

$$6\ Na_2S_2O_3 \equiv KIO_3.$$
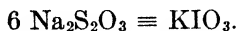
The molarity of the sodium thiosulfate solution should be calculated from the mean of triplicate calculations.

380. Standardization by Resublimed Iodine. — Iodine must always be sublimed twice prior to its use as a primary standard. The first sublimation is effected in the presence of added potassium iodide in order to get rid of any chlorine and bromine which might be present; at the same time, any non-volatile contaminants will be eliminated, while the moisture, which is almost invariably present in every sample of iodine, will be very greatly reduced if the proper technique is followed.[8] The resublimation is effected without the addition of any potassium iodide in order that any potassium iodide carried over in the first distillation as well as any fresh iodide shall not be carried over into the final product.

For the first sublimation, the iodine should be mixed in an agate mortar with about one-fifth of its weight of potassium iodide. The mixture is then transferred to a watch-glass and the latter is placed on a piece of asbestos board having a hole cut in the center, so that gentle heat can be supplied by the small flame of a Bunsen burner. A second watch-glass, somewhat larger than the first,[9] is now placed, with its concave side down, on top of the first watch-glass and is covered with a small piece of wet towel to keep it cool. Gentle heat is applied and, after a considerable portion of iodine has condensed, the top watch-glass is removed and another watch-glass similar to it and covered with a piece of wet towel is put in its place. The sublimation is continued until about three-fourths (but not all) of the iodine has been sublimed. The iodine so collected is submitted to a second sublimation, but without the addition of any potassium

[8] C. W. Foulk and S. Morris, *J. Am. Chem. Soc.*, **44**, 228 (1922).

[9] This facilitates its easy handling later in the operation.

iodide. The finally purified product is immediately transferred
to a small glass-stoppered bottle which has been thoroughly cleaned
and dried.

Weighing out Portions of Iodine. — Iodine should never be intro-
duced directly into the balance case because its fumes will attack
and corrode the metallic parts of the balance. The method given
by Treadwell-Hall,[10] and quoted almost verbatim herewith,
should be used. In each of two or three small weighing-tubes
with tightly fitting glass stoppers are placed 2–2.5 g. of pure
potassium iodide free from iodate and 0.5 ml. of water (not more);
the tubes are stoppered and accurately weighed by the method of
swings. The tubes are then opened and 0.3–0.4 g. of pure iodine
is added to each. The tubes are quickly stoppered and again
weighed; the difference shows the amount of iodine. The iodine
dissolves almost instantly in the concentrated potassium iodide
solution. One of the tubes is then placed in the neck of a 500 ml.
Erlenmeyer flask which is held in an inclined position and con-
tains 200 ml. of water and about 1 g. of potassium iodide. The
tube is dropped to the bottom of the flask, but just as it begins to
fall the stopper is removed and allowed to follow it. In this way
there is no iodine lost, which will be the case if the contents of a
tube are washed into the water. A solution is thus prepared con-
taining a known amount of iodine and to it the sodium thiosulfate
solution which is to be standardized is added from a burette until
the liquid is pale yellow in color. Now, 2–3 ml. of starch solution
is added and the solution carefully titrated until it becomes color-
less. From the mean of three determinations, the strength of
the thiosulfate solution is calculated.

381. *Standardization by Metallic Copper.* — In acetic acid
solution, cupric ion and iodide ion react to form iodine and cuprous
ion, the latter being precipitated out of solution as the insoluble
cuprous iodide, the mechanism of the reaction being represented
by the scheme:

$$2 \, Cu^{++} + 2 \, I^- \rightarrow 2 \, Cu^+ + I_2$$
$$2 \, I^- \text{ (in excess)}$$
$$\downarrow$$
$$2 \, CuI$$
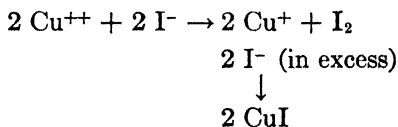
[10] Treadwell-Hall, p. 600 of reference given in § 11.

The reaction is quantitative and can be used as the basis of the standardization of sodium thiosulfate solutions.   It is important in using this reaction to observe that the anion of any strong acid, *i.e.*, sulfate ion, chloride ion, nitrate ion, etc., must be excluded, except for very small quantities, as the presence of such ions prevents, more or less completely, the quantitative precipitation of the cuprous ion.   The quantitative precipitation of cuprous iodide is absolutely essential in order that the reduction of the cupric ion be quantitative.   Furthermore, there should not be present any other oxidizing agent than the cupric ion, or any other reducing agent than the iodide ion, for the first would liberate iodine and cause too high results, while the second would reduce some of the liberated iodine and cause low results.

A strip of pure copper foil should be thoroughly cleaned and three pieces, each weighing about 0.150 g., should be cut from it. The three pieces are dissolved in separate small beakers by treating each with about 5 ml. of 8 *M* nitric acid.   Each beaker is placed on a water-bath or steam hot-plate, and evaporated to the point at which the solution will just solidify upon cooling.   Care must be taken, however, not to evaporate too far as such over-evaporation will produce basic salts of copper which are very difficult to dissolve.   The copper nitrate is dissolved in about 15 ml. of cold water, and a 1 *M* solution of sodium hydroxide is added, dropwise, until a slight permanent precipitate of cupric hydroxide forms.   About 5 ml. of 8 *M* acetic acid is added and the solution is diluted with cold water to about 50 ml.   Then 10 ml. of 1.8 *M* potassium iodide solution is added to the contents of the first beaker.   It is allowed to stand for about 30 seconds, after which it is titrated immediately with the sodium thiosulfate solution until the brown color has changed to a light yellow.   Then 3 ml. of starch solution is added, and the titration is continued with constant stirring until the blue color disappears.   This blue color will return, more or less quickly, upon standing,[11] but the end point is to be taken as its first complete disappearance.   The

[11] Large amounts of sodium acetate cause a quick return of the blue color. Therefore, care should be taken to add not more than a few drops excess of sodium hydroxide solution in neutralizing the nitric acid which remains after evaporation.

contents of the second and third beakers are treated in a similar manner, and from the mean of the three determinations the value of the thiosulfate solution is calculated.

382. Exercise No. 43.   Preparation and Standardization of 0.1 M Sodium Thiosulfate Solution. — Prepare an approximately 0.1 M solution of sodium-thiosulfate and determine its exact value by one of the preceding methods.

383. Exercise No. 44.   Iodimetric Determination of Copper in an Ore. — Weigh out from 0.5 to 1 g. of the finely ground ore,[12] and transfer it to a covered casserole.   Add about 20 ml. of 16 M nitric acid, 5 ml. of 12 M hydrochloric acid, and 5 ml. of 18 M sulfuric acid.   Heat until the decomposition of the ore is complete, remove the cover and evaporate to dense fumes of sulfur trioxide.   Continue the evaporation to a volume of 5 ml.   Cool, add carefully about 40 ml. of water, and heat to dissolve soluble salts.   Filter through a small filter and wash with hot water.

Most ores are completely decomposed by the above treatment. Certain silicates, slags, etc., require a sodium carbonate fusion of the residue from the acid treatment.   In case fusion is necessary, lead sulfate, if present in the residue, must first be removed by repeated treatment with hot 3 M sodium acetate solution.   Silver chloride, if present, must be removed by repeated treatment of the residue with hot 6 M ammonium hydroxide solution.   Fuse the residue, which has been freed from lead and silver salts, with sodium carbonate and decompose the fused mass with hydrochloric acid in the usual manner.   Then add 5 ml. of 18 M sulfuric acid to the solution, and evaporate the latter to fumes of sulfur trioxide as above.   Dissolve the soluble salts in water, filter, and add the filtrate and washings to the main solution.   If silver is present in the main solution, remove it by precipitation as chloride and filter.   Then evaporate to fumes of sulfur trioxide, after the addition of sulfuric acid, as described above.

The volume of the solution should now be about 100 ml. and the concentration of sulfuric acid about 1 M.   If the acid is more concentrated than this, the excess must be neutralized by am-

[12] This weight of sample presupposes that the copper content is between 15% and 30%; if the copper content happens to be under or above these percentages, a proportionately larger or smaller weight of sample must be taken accordingly.

monium hydroxide; if less concentrated, the proper volume of 18 M sulfuric acid must be added.   Place in the solution two pieces of sheet aluminum, about 1.5 inches square and with the corners turned over so that the pieces are held away from the bottom of the beaker.   Cover with a watch-glass and boil the solution for about 15 minutes.   Copper and other metals of lower solution tension than iron will be deposited.   Among such elements, the only ones likely to be encountered here are lead, cadmium, bismuth, arsenic, and antimony.   Decant at once through a 9 cm. filter paper and wash thoroughly with boiling water, keeping the aluminum and as much of the copper as possible in the beaker. Add about 10 ml. of 8 M nitric acid to the beaker containing the aluminum and copper, and warm until all the copper has been dissolved.   Pour this warm solution through the filter in such a manner as to dissolve any particles of copper it may contain and receive the filtrate in a small beaker.   Wash the original beaker, the aluminum and the filter paper two or three times with a very small amount of water.   When the solution has drained from the funnel, remove the beaker and place a small watch-glass under the funnel to receive any further drops of solution that may run through the funnel.   To the copper solution, add about 30 ml. of bromine water and boil to oxidize any arsenic and antimony that may be present.   Continue the boiling until all excess bromine is expelled.   Again place the beaker under the funnel, wash any solution from the watch-glass into the beaker and complete the washing of the filter paper with hot water.   Evaporate the solution on the water-bath or hot-plate until it just solidifies upon being removed and is allowed to cool somewhat; then complete the determination exactly as described for the standardization of the thiosulfate solution.   Bismuth and lead, if present, are without effect upon the titration except that the color change in this case is from a greenish color to a pale yellow instead of from blue to colorless.   From the data obtained, and an auxiliary determination of the moisture content of the sample, calculate the percentage of copper in the ore on the dry basis.

384. Exercise No. 45.   Iodimetric Determination of Copper in German Silver. — Before weighing, the sample should be carefully inspected and freed from foreign matter and products of

corrosion. Weigh out about 0.45 g. of sample and place it in a 250 ml. beaker. Add 40 ml. of 8 M nitric acid and cover with a watch-glass. Heat cautiously if necessary. When solution is complete, wash down the sides of the beaker and the watch-glass with distilled water, cool, and add 12 ml. of 9 M sulfuric acid. Evaporate till fumes of sulfur trioxide are evolved and continue the evaporation to a volume of 5 ml. Cool and dilute with distilled water to about 80 ml. Wash the lower side of the watch-glass and the sides of the beaker with distilled water and dilute to 100 ml. with distilled water. At this point, the concentration of sulfuric acid should be about 1 M. Place in the solution two pieces of sheet aluminum, about 1.5 inches square and with the corners turned over so that the pieces are held away from the bottom of the beaker. Proceed from this point exactly as in the determination of copper in copper ore, described in the preceding paragraph.

385. Standard Iodine Solution. — Although iodine is only slightly soluble in water, it can be dissolved in relatively large amounts in solutions containing the iodide ion, due to the reaction,

$$I_2 + I^- \rightleftarrows I_3^-.$$
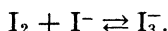
When the iodine in the solution is used as an oxidant in a titration, the above equilibrium is displaced to the left due to the reduction of the iodine in accordance with the following equation,

$$2 e + I_2 \rightarrow 2 I^-.$$
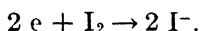
Iodine solution can be standardized against arsenous oxide.[13] The arsenous oxide is dissolved in a solution of sodium hydroxide, after which the solution is neutralized with sulfuric acid using methyl orange as the indicator, and then it is made slightly alkaline by adding sodium bicarbonate. The change undergone by the arsenous oxide may be represented as follows,

$$As_2O_3 + 3 H_2O \rightarrow 2 H_3AsO_3.$$
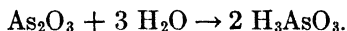
On titrating with iodine solution, the arsenous acid is oxidized, as shown in the following equation,

$$I_2 + H_3AsO_3 + H_2O \rightarrow H_3AsO_4 + 2 I^- + 2 H^+.$$
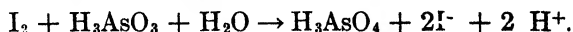
[13] Chapin, *J. Am. Chem. Soc.*, **41**, 351 (1919).

If the hydrogen ions produced by this reaction were permitted to accumulate in the solution, equilibrium might be established before the reaction had become quantitative. To avoid this error, bicarbonate ions are added before beginning the titration to serve as a buffer and prevent too great an accumulation of hydrogen ions. The end point of this titration is the appearance, in the presence of starch solution, of a faint blue color.

After standardizing, this solution should be stored in a dark place since light catalyses the oxidation of iodide ion to iodine by the oxygen of the air.

386. Exercise No. 46. Preparation of 0.1 M Iodine Solution and Standardization against Arsenous Oxide. — Prepare 25 ml. of 10 M KI solution. Weigh on the rough laboratory balance 12.7 g. of iodine and dissolve it in the potassium iodide solution, with stirring but without the application of heat. When all the iodine has dissolved, dilute the solution to one liter with distilled water.

In order to standardize this solution, weigh out triplicate samples of pure, dry As_2O_3 weighing from 0.25–0.30 g. Dissolve each in 15 ml. of molar NaOH solution in an Erlenmeyer flask. Add molar H_2SO_4 until the solution is just acid to methyl orange and then add 60 ml. of 0.5 M Na_2CO_3 solution. Add 3 ml. of a 1 % starch solution, wash down the sides of the flask with a little distilled water from the wash bottle and titrate with the iodine solution. The end point is the appearance of a faint blue color. From the results of the triplicate titrations, calculate the molarity of the iodine solution. Store in a cool, dark place.

387. The Iodimetric Determination of Antimony. — On dissolving a sample containing trivalent antimony, it is necessary to form a complex ion with the Sb^{+++} in order to prevent the precipitation of SbOCl as a result of hydrolysis. This can be conveniently effected by dissolving the sample in concentrated HCl solution. The reaction involved is

$$Sb^{+++} + 6\ Cl^- \rightleftarrows SbCl_6^{\equiv}.$$

After completely dissolving the sample, the solution is heated to remove any sulfide ion, so that on subsequent dilution Sb_2S_3 will not precipitate. Dilution would also cause SbOCl to precipitate and hence, before diluting, it is necessary to convert the complex

chloride ion into the more stable antimonyl tartrate ion by the addition of tartrate ion.   Thus,

$$SbCl_6^{\equiv} + C_4H_4O_6^{=} + H_2O \rightarrow SbO(C_4H_4O_6^{-}) + 2\,H^+ + 6\,Cl^-.$$
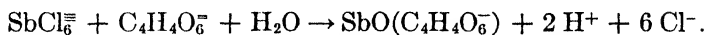
The $SbO(C_4H_4O_6^{-})$ is then titrated with standard iodine solution,

$$SbO(C_4H_4O_6^{-}) + I_2 + H_2O \rightarrow SbO_2(C_4H_4O_6^{-}) + 2\,H^+ + 2\,I^-.$$
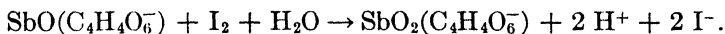
Since the hydrogen ions liberated by this reaction might bring about equilibrium before the reaction becomes quantitative, the solution is buffered with bicarbonate ions before beginning the titration.

388. Exercise No. 47.   Determination of Antimony in an Antimonous Sulfide Ore. — Weigh out into beakers triplicate samples of the ore containing between 0.3 and 0.4 g. of antimony. Cover each beaker with a watch-glass, add 25 ml. of 12 M HCl to each and digest at room temperature for 15 minutes.   Place on the steam bath until the antimony has been dissolved and all the hydrogen sulfide has been expelled.   Add 3 g. of tartaric acid dissolved in about 5 ml. of distilled water and heat on the steam bath for 5 minutes.   Cool, add 100 ml. of distilled water and neutralize with 6 M NH₄OH.   Add 5 g. of NaHCO₃, then 3 ml. of a 1% starch solution, and titrate with standard iodine solution until the solution acquires a blue color.

From the results of triplicate titrations and a determination of moisture, performed on a separate portion of the sample, calculate the per cent of antimony in the ore on the dry basis.

389. Examples.

1. 20.61 ml. of KMnO₄ solution was found to be equivalent to 0.3101 g. of Na₂C₂O₄.   27.28 ml. of the same KMnO₄ solution was added to KI solution and the iodine liberated was then titrated with 42.10 ml. of Na₂S₂O₃ solution.   Calculate the molarity of the Na₂S₂O₃ solution.

2. The lead in a 2.1020 g. sample of an alloy was precipitated quantitatively as PbCrO₄.   This precipitate was dissolved in HCl and excess KI solution was added.   The iodine formed was then titrated with 21.32 ml. of 0.05215 M Na₂S₂O₃ solution.   Calculate the per cent of Pb in the alloy.

3. A solution of 2.0700 g. of a salt mixture containing Pb(NO₃)₂ and KNO₃ was treated with 50.00 ml. of a solution of K₂Cr₂O₇, one milliliter of which is equivalent to 6.0 mg. of Fe.   The excess K₂Cr₂O₇ was then titrated iodimetrically with 35.00 ml. of 0.005001 M Na₂S₂O₃ solution. Calculate the per cent of Pb(NO₃)₂ in the sample.

CHAPTER XIX

THEORY OF ELECTRODEPOSITION

390. Electrolysis. — Electrolytic determinations are based upon the fact that when a direct current of electricity is caused to pass through a solution of an electrolyte, there always results an oxidation of some of the negatively charged ions present and a reduction of some of the posi-tively charged ions present. This phenomenon is known as *electrolysis*. The conductor which is attached to the nega-tive terminal of the source of current, and by means of which electrons enter the solution, is known as the *cathode* (Figure 76). The conductor which is attached to the positive ter-minal of the source of current, and by means of which the electrons leave the solution, is known as the *anode*. The anode and the cathode are often spoken of simply as the electrodes.
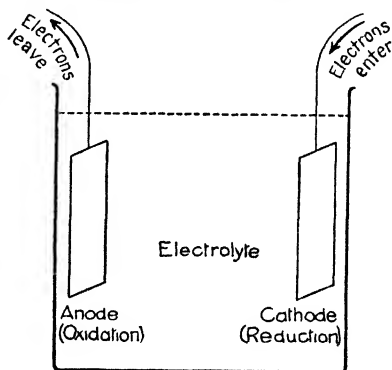
Fig. 76
Electrolytic Cell

The respective oxidations and reductions never take place in the mass of the solution itself but only at the electrodes, oxidation taking place at the anode, reduction at the cathode. Moreover, for each amount of substance oxidized at the anode, there is always an exactly equivalent amount of substance simultaneously reduced at the cathode in accordance with Faraday's Law that for each 96,500 coulombs of electricity passed through an electrolyte, one gram equivalent of substance is oxidized at the anode and one gram equivalent of substance is reduced at the cathode.

It is to be further noted that the various kinds of anions are not all oxidized with the same ease. The relative order of some of

these, with the most easily oxidized coming first, is sulfide, hydroxyl, iodide, bromide, chloride, and sulfate ions. Similarly, the various kinds of cations are not all reduced with the same ease. The relative order of some of these, with the most easily reduced coming first, is auric, platinic, silver, mercurous, cupric, arsenous, bismuth, antimonous, hydrogen, lead, stannous, zinc, magnesium, and sodium ions.

The electrolysis of a solution is thus seen to be a special case of oxidation-reduction because we have the oxidation of one species of ion taking place at the anode simultaneously with the reduction of another species of ion at the cathode. There are, however, certain features beyond those already developed in Chapter XV in regard to the general theory of oxidation-reduction reactions which have to be considered. These features deal with the relationship that the impressed e.m.f. bears to the action at the electrodes and to the flow of current through the electrolyte.

391. Theoretical Decomposition Voltage. — In order to study some of the important features of electrolysis, let us suppose that we have as our electrolyte a solution which is 0.02 M with respect to cupric ion, and 0.8 M with respect to hydrogen ion. These are concentrations frequently employed in the electrolytic deposition of copper in analytical procedure. Now let us suppose that we introduce two platinum electrodes into the solution and connect them with a small external potential difference of about 0.2 volts. A momentary current will flow during the passage of which cupric ions will be reduced at the cathode in accordance with the equation,

$$4 e + 2 Cu^{++} \rightarrow 2 Cu°,$$
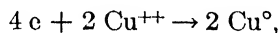
and hydroxyl ions will be oxidized at the anode as illustrated by the equation

$$4 OH^- \rightarrow O_2 + 2 H_2O + 4 e,$$

thereby establishing the cupric-copper system at the cathode and the oxygen-hydroxyl ion system at the anode. During the passage of the current, the cupric ion concentration is decreased and the potential of the cupric-copper system is lowered. Decrease in the hydroxyl ion concentration, with the attendant increase in the oxygen concentration, raises the potential of the oxygen-

hydroxyl ion system. It should be kept in mind that as the difference in potential between the cupric-copper and oxygen-hydroxyl systems increases, the tendency for electrons to flow from the metallic copper through the external circuit to the oxygen also increases. This is opposite to the direction of flow of current from the external difference of potential. In other words, a counter electromotive force is set up within the cell in opposition to the impressed electromotive force. When this counter electromotive force increases until it is equal to the external difference of potential, the current ceases to flow. The counter electromotive force is equal to the difference between the potentials of the oxygen-hydroxyl ion system and the cupric-copper system. That is,

$$\text{Counter e.m.f.} = e_{O_2, \text{OH}^-} - e_{\text{Cu}^{++}, \text{Cu}}$$

where e_{O_2, OH^-} and $e_{\text{Cu}^{++}, \text{Cu}}$ are the potentials of the oxygen-hydroxyl ion system and the cupric-copper system, respectively.

If now the external potential difference is increased from 0.2 volts to 0.4 volts, current will flow momentarily as before until the counter electromotive force has again increased sufficiently to prevent its flow. If we keep on stepping up our external difference of potential by regular intervals, we will finally reach a point at which the solution becomes saturated with oxygen and the copper deposited on the cathode is sufficient in quantity to function as a pure copper electrode. When the external difference of potential is increased beyond this point, the counter electromotive force will fail to increase sufficiently to stop the flow of current. The potential difference, which must be exceeded in order to cause an infinitesimal current to flow continuously, is known as the *theoretical decomposition voltage*. When this potential
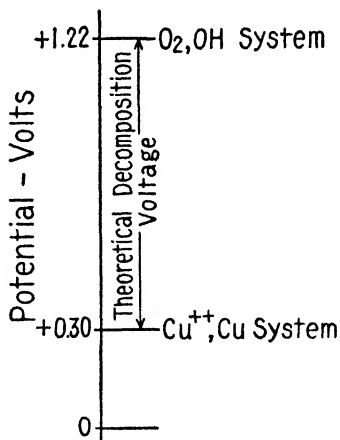

Fig. 77

Theoretical Decomposition Voltage for Solution $0.02M$ with Respect to Cupric Ion and $0.8M$ with Respect to Hydrogen Ion

is reached, the equilibrium potential of each of the systems may be expressed by the Nernst equation as follows:

$$e_{O_2,\ OH^-} = \frac{0.0001983\ T}{4} \log \frac{[O_2]}{[OH^-]^4 K_{O_2,\ OH^-}}$$

$$e_{Cu^{++},\ Cu} = \frac{0.0001983\ T}{2} \log \frac{[Cu^{++}]}{K_{Cu^{++},\ Cu}}$$

and the theoretical decomposition voltage E' is obtained as follows:

$$E' = e_{O_2,\ OH^-} - e_{Cu^{++},\ Cu} = \frac{0.0001983\ T}{4} \log \frac{[O_2]}{[OH^-]^4 K_{O_2,\ OH^-}}$$

$$- \frac{0.0001983\ T}{2} \log \frac{[Cu^{++}]}{K_{Cu^{++},\ Cu}}.$$

For the case in hand, in which the solution is 0.02 M with respect to cupric ion, and 0.8 M with respect to hydrogen ion, and from which the oxygen is liberated at one atmosphere of pressure, the potential of the oxygen-hydroxyl ion system is,

$$e_{O_2,\ OH^-} = -\frac{0.0001983\ (273 + 25)}{4} \log \frac{1}{(1.2 \times 10^{-14})^4 \times 1 \times 10^{-27}}$$

$$= 1.22 \text{ volts,}$$

and the potential of the cupric ion-copper system is

$$e_{Cu^{++},\ Cu} = \frac{0.0001983\ (273 + 25)}{2} \log \frac{2 \times 10^{-2}}{2 \times 10^{-12}} = 0.30 \text{ volts.}$$

The theoretical decomposition voltage, E', is then

$$E', = e_{O_2,\ OH^-} - e_{Cu^{++},\ Cu} = 1.22 - 0.30 = 0.92 \text{ volts.}$$

These relationships are shown diagrammatically in Figure 77.

392. Overvoltage. — It has been found by experiment that, in general, as we increase the external difference of potential above the value of the theoretical decomposition voltage until the products of reaction are being liberated at an appreciable rate, the value of the external difference of potential E required to

produce the current I is obtained, in accordance with the generalized form of Ohm's Law, from

$$E = E' + IR + E''.$$

In the above equation, E' is the theoretical decomposition voltage, IR is the voltage drop through the resistance R of the solution in the cell, and E'' is an additional voltage which must be overcome, known as *overvoltage*.

Before discussing the variables involved in overvoltage, it will be convenient to state at this point that the current per unit of electrode surface is referred to as *current density* and may be expressed in amperes per square centimeter. In estimating the area of a thin sheet electrode, both sides of the conductor are considered; thus, if the dimensions are 8.0 cm. × 5.0 cm., the area is 80.0 cm.^{2} When a current of 0.8 amp. is used, the current density will be 0.01 amp./cm.^{2}

It has been shown that the overvoltage effect is resolvable into one effect at the anode and another effect at the cathode; we thus speak of anodic overvoltage and cathodic overvoltage. In general, overvoltage, either at the anode or cathode, is a function of the following variables:[1]

1. The nature of the ion being deposited.

2. The metal that is used for an electrode, whether platinum, iron, copper, etc.; its purity and the physical condition of its surface.

3. The physical state in which the ion comes out at the electrode when it is discharged. If it appears as a metal, the overvoltage is often very small; if as a gas, however, the overvoltage is relatively very great.

4. The current density employed. Increase in current density means increase in overvoltage; for current densities from 0.00005 amp./cm.^{2} up to 0.01 amp./cm.^{2}, the increase in overvoltage is very rapid; beyond current densities of 0.01 amp./cm.^{2}, the increase in overvoltage still continues, but far less rapidly.

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[1] For a very thorough discussion of the subject of overvoltage, the reader is referred to A. J. Allmand and H. J. T. Ellingham, "The Principles of Applied Electrochemistry," 2nd ed., p. 73 *et seq.*, Longmans, Green & Co., New York, 1931.

5. The concentration gradient existing around the electrodes. As this increases, the overvoltage rises. The addition of a colloid in small quantity increases the viscosity of the solution and thereby increases the concentration gradient and the overvoltage. Stirring of the solution lowers the concentration gradient and consequently lowers the overvoltage.

6. The temperature of the solution.[2] Increase in temperature decreases the overvoltage because it helps in keeping down the concentration gradient at an electrode by virtue of the convection currents which it produces in the solution and by virtue of the increased mobility which it imparts to the ions.

Table 57 gives the cathodic overvoltages for copper when deposited from a slightly acid solution of copper sulfate at 20°

Table 57

OVERVOLTAGES FOR COPPER AND ION WHEN DEPOSITED FROM SLIGHTLY
ACID SOLUTION

Current Density	Cathodic Overvoltage	
(Amp./cm.²)	Cu^{++} on Cu	Fe^{++} on Fe
0.00006	....	0.108
0.00011	0.011	0.129
0.00227	0.013	0.141

as compared with those for the deposition of iron from a slightly acid solution of ferrous sulfate under similar conditions.[3]

The cathodic overvoltages of hydrogen from acid solution, when various cathode materials are used at various current densities and when dilute sulfuric acid (up to 1 M) is used as the electrolyte, and the electrolysis is conducted at room temperature,[4] are given in Table 58 and are shown graphically in Figure 78.

[2] Knobel and Joy, *Trans. Electrochem. Soc.*, **44**, 443 (1923):
[3] Quoting Allmand and Ellingham, p. 112 of reference cited above. These authors quote as their authority, Foerster and Mustad, *Abhand. Bunsen Ges.*, **2**, 44 (1909).
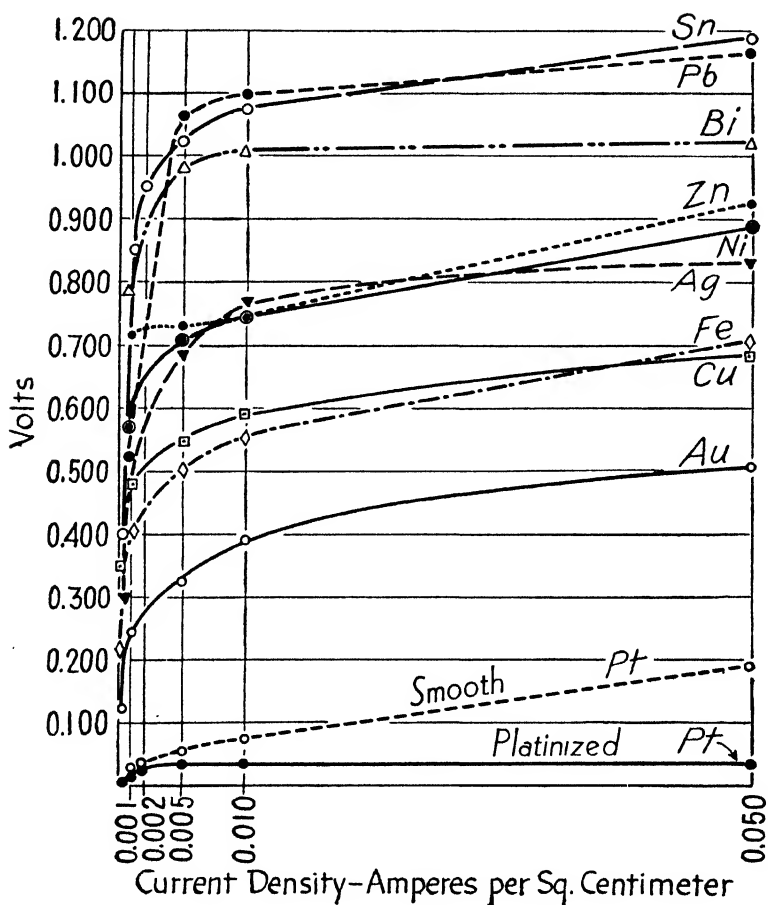[4] Knobel, Caplan, and Eiseman, *Trans. Electrochem. Soc.*, **43**, 55 (1923).

Fig. 78

Hydrogen Overvoltages in Acid Solution at 25°

Table 58

Cathodic Overvoltage for Hydrogen in Acid Solution (Volts) at 25°

Nature of Cathode	Current Density (Amp./cm.²)					
	0.0001	0.001	0.002	0.005	0.010	0.050
Platinized platinum........	0.0034	0.0154	0.0208	0.0272	0.0300	0.0376
Smooth platinum..........	....	0.024	0.034	0.051	0.068	0.186
Gold	0.122	0.241	....	0.332	0.390	0.507
Copper	0.351	0.479	....	0.548	0.584	0.68*
Silver....	0.298	0.475	0.579	0.692	0.762	0.830
Tin.....................	0.399	0.856	0.947	1.026	1.077	1.185
Iron....................	0.218	0.404	0.447	0.502	0.557	0.700
Zinc....................	....	0.716	0.726	0.726	0.746	0.926
Bismuth.................	....	0.780	....	0.980	1.05	1.15
Nickel..................	....	0.563	0.633	0.705	0.747	0.890
Lead...................	....	0.52	....	1.060	1.090	1.168
Cadmium................	0.651	0.981	....	1.086	1.134	1.211

* Interpolated value.

The cathodic overvoltages of hydrogen from alkaline solution, when various cathode materials are used at a current density of 0.01 amp./cm.², when 1 M sodium hydroxide solution is used as the electrolyte, and the electrolysis is conducted at room temperature,[5] are given in Table 59.

Table 59

Cathodic Overvoltage for Hydrogen in Alkaline Solution (Volts)

Nature of Cathode	Current Density (Amp./cm.²) 0.01
Platinum...............	0.54
Silver.................	0.61
Copper................	0.91
Tin...................	0.94
Iron..................	0.54
Zinc.................	1.05

[5] Glasstone, *Trans. Chem. Soc.*, **123**, 1745 (1923).

For the anodic overvoltage of oxygen in acid solutions, the figures which are given in the literature are not very numerous; for smooth platinum in a solution about 0.8 M with respect to hydrogen ion at 25° with a current density of 0.05 amp./cm.², it may have a value of 1.2 volts or less, depending on the purity of the anode surface, its physical condition, and the duration of electrolysis.
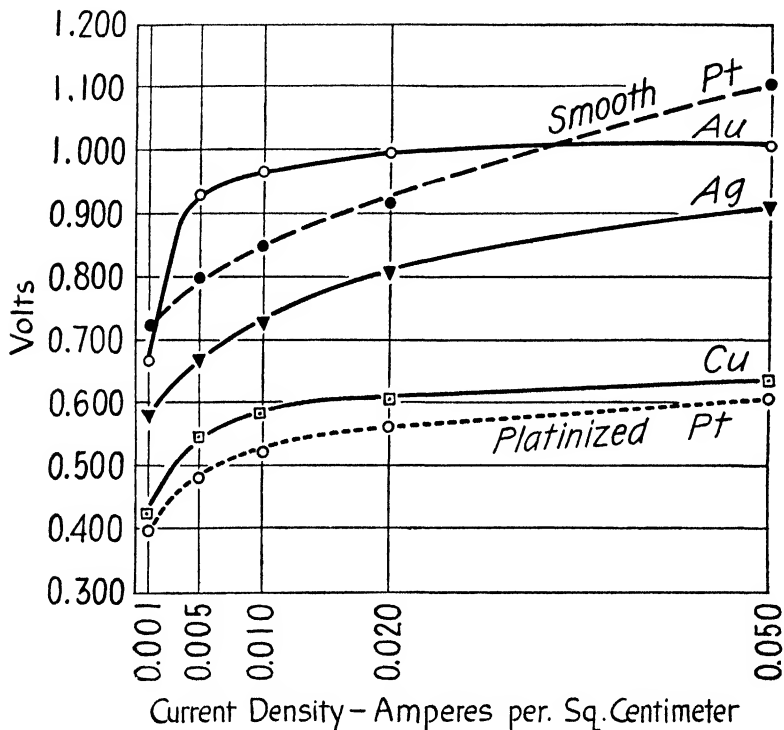

Fig. 79

Oxygen Overvoltages in Alkaline Solution at 25°

The anodic overvoltages of oxygen in alkaline solution,[6] for various anode materials at various current densities when 1 M potassium hydroxide is used as the electrolyte and the electrolysis is conducted at 25°, are given in Table 60 and are shown graphically in Figure 79.

[6] Knobel, Caplan and Eiseman, *Trans. Electrochem. Soc.*, **43**, 55 (1923).

Table 60

ANODIC OVERVOLTAGES FOR OXYGEN IN ALKALINE SOLUTION* (VOLTS) AT 25°

Nature of Anode	Current Density (Amp./cm.²)				
	0.001	0.005	0.010	0.020	0.050
Platinized platinum.....	0.398	0.480	0.521	0.561	0.605
Smooth platinum.......	0.721	0.80	0.85	0.92	1.16
Gold.................	0.673	0.927	0.963	0.996	1.064
Copper...............	0.422	0.546	0.580	0.605	0.637
Silver................	0.580	0.674	0.729	0.813	0.912

*It is to be noted that oxygen overvoltage increases very rapidly for the first 60 minutes or so, and then increases more or less slowly for a considerable number of hours. The values given here are those taken after one minute.

393. External Difference of Potential Required at the Beginning of the Electrolysis. — In order to facilitate the consideration of the external difference of potential required in electrolysis, let us select as an illustration the same copper sulfate solution referred to in § 391. The external difference of potential E required at the beginning of the electrolysis is obtained from

$$E = (e_{O_2, OH^-} - e_{Cu^{++}, Cu}) + (\xi_{O_2} + \xi_{Cu}) + IR$$

where the quantity $(e_{O_2, OH^-} - e_{Cu^{++}, Cu})$ is the theoretical decomposition voltage of the cell, the quantity $(\xi_{O_2} + \xi_{Cu})$ is the sum of the cathodic and anodic overvoltages or the overvoltage of the cell, and IR is the voltage required to overcome the resistance R of the cell. Let us assume that R is 0.20 ohms, the temperature is 25°, the area of the cathode (Figure 85) is 80.0 cm.², the area of the anode is 16.0 cm.², and that the cathodic current density desired is 0.01 amp./cm². The current I required will be 80.0 × 0.01 or 0.8 amp. and the anodic current density will be 0.8 ÷ 16 or 0.05 amp./cm.² Under these conditions, let us assume that the oxygen overvoltage is 1.16 volts and that the overvoltage of the copper is negligible. The external difference of potential required is then,

$$E = (1.22 - 0.30) + (1.16 + 0.0) + 0.8 \times 0.20 = 2.23 \text{ volts.}$$

As electrolysis proceeds, the decrease in concentration of cupric ion causes the potential of the cupric ion-copper system to become less positive, and consequently causes an increase in the external difference of potential which must be applied in order to continue to deposit copper at the cathode and oxygen at the anode. To calculate the total voltage required toward the end of the electrolysis when the concentration of copper in solution has been diminished to about 1×10^{-4} moles per liter, we proceed as above, except that in considering the potentials at the cathode, we have to take cognizance of the fact that hydrogen may be plated out there as well as copper. It, therefore, becomes necessary to investigate the phenomenon of the simultaneous deposition of two different kinds of ions.

394. Simultaneous Deposition of Two Different Kinds of Ions. —Whenever there is a possibility of two different kinds of ions being discharged at the same electrode, the answer as to which kind will be deposited is found in the rule of Le Blanc, that *that kind of ion will be discharged which requires the least expenditure of electrical energy, taking account of both the equilibrium potential and the overvoltage potential associated with the discharge.* When it so happens that the energy required to effect the discharge of one kind of ion at a given electrode is equal to the energy required for the discharge of another kind of ion at the same electrode, then both kinds of ions will be simultaneously discharged. This rule applies alike to actions at the cathode and at the anode.

395. *Application of Le Blanc's Rule to Cation Discharge.* — The algebraic sum of the equilibrium potential and the over-voltage potential for an ion is a measure of the electrical energy required for discharge at the electrode. It follows, in terms of the zero potential which we have adopted, that that cation will be discharged first for which the algebraic sum of the equilibrium potential and the overvoltage potential is less negative or more positive. We shall speak of this sum as the *deposition potential* of an ion.

Let us apply this rule to the deposition of the cupric ion and the hydrogen ion in the electrolysis of the cupric solution considered in § 391. As the cupric ion concentration becomes smaller, with the consequent lowering of the equilibrium potential of the cupric

copper system on the scale of potentials, the deposition potential of copper will also be lowered, since it is the algebraic sum of the equilibrium potential and the overvoltage for copper. The extent to which the deposition potential is lowered will depend on two factors: (1) the extent to which the cupric ion concentration is diminished, and (2) the magnitude of the overvoltage for copper. At the beginning of the electrolysis the overvoltage for copper is so small that it is negligible, but for the extremely dilute solution of cupric ion with which we are concerned toward the end of the electrolysis, this overvoltage may be considerable, with the result that the deposition potential of copper may be much lower on the scale of potentials than the equilibrium potential of the cupric-copper system. The copper overvoltage is increased by an increase in current density and is decreased by stirring the solution. With current densities frequently employed in electrolytic methods, and in spite of the fact that the solution is rapidly stirred, the deposition potential of copper may drop on the scale of potentials to a value equal to that of the deposition of hydrogen. When this occurs, codeposition of copper and hydrogen will take place. Let us now consider some of the factors which determine the deposition potential of hydrogen.

During the deposition of copper at the cathode, hydroxyl ions have been removed from the solution at the anode and, consequently, there has been an increase in the hydrogen ion concentration of the solution. For solutions like the one under consideration, which is strongly acid and contains a relatively small concentration of cupric ion, the increase in hydrogen ion concentration during electrolysis is negligible. For the case in hand, we can consider that the equilibrium potential of the hydrogen ion-hydrogen system is

$$e_{H^+, H_2} = 0.0001983 \, T \log [H^+] = 0.0001983 \, (273 + 25) \log 8 \times 10^{-1}$$

$$e_{H^+, H_2} = - \, 0.006 \text{ volts, or approximately } 0.01 \text{ volts.}$$

It follows that the deposition potential of hydrogen is more negative than $- 0.01$ by the amount of the hydrogen overvoltage which we will assume is about 0.58 volts, and consequently has a value of $- 0.59$ volts. When the deposition potential of copper

has been diminished to this value, simultaneous deposition of copper and hydrogen will take place. This is illustrated in Figure 80.

It is to be pointed out that the reducing action of the electric current at the cathode is not restricted to cases where the dis-charged ion appears either as a de-posited metal or as a liberated gas; the reducing action also may effect the reduction of an ion from one ionic state to another. Thus, if the deposition potential at the cathode becomes less positive or more negative, nitrate ion may be reduced to nitrite ion or if ferric ion is present, it may be reduced to ferrous ion. Toward the end of the electrolysis of a cupric solution containing much iron, most of the current is carried by the iron so that quantitative deposition of the copper may require a very long time. If the current density is increased
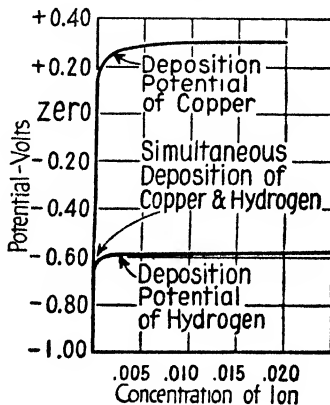
Fig. 80

Deposition Potentials of Cop-per and Hydrogen

in order to shorten the time required, the deposition potential of copper will be lowered on the scale of potentials with the possi-bility that hydrogen may be evolved. The evolution of hydrogen should be diminished to a minimum as it tends to produce a non-adherent copper deposit.

In the determination of copper in solutions containing nitrate ion, nitrite ion formed at the cathode may introduce serious error by preventing quantitative deposition of copper. By adding hydrogen peroxide to the solution for the purpose of oxidizing nitrite ion back to nitrate ion, the deposition of copper can be made more nearly quantitative (§ 415).

396. *Application of Le Blanc's Rule to Anion Discharge.* — For anion discharge, Le Blanc's rule assumes the form that that anion will be discharged first for which the algebraic sum of the equilibrium potential and the overvoltage potential is less positive or more negative. Thus, if the equilibrium potentials of the

[481]

chlorine-chloride, bromine-bromide and iodine-iodide systems in a given solution are $+ 1.55$, $+ 1.20$ and $+ 0.80$ volts, respectively, and the overvoltages of chlorine,[7] bromine and iodine at a smooth platinum anode at room temperature and at a current density of 0.05 amp./cm.² are, respectively, 0.045, 0.01 and 0.01 volts, then the corresponding deposition potentials will be $+ 1.59$, $+ 1.21$, and $+ 0.81$ volts. Under these conditions iodine will deposit before bromine and bromine will deposit before chlorine.

It is to be pointed out that the oxidizing action of the electric current at the anode is not restricted to cases where the discharged ion appears as a liberated gas; the oxidizing action may also effect the oxidation of an ion from one state of oxidation to another. Thus, in nitric acid solution, manganous ion may be oxidized to the acid manganite ion, which precipitates out on the anode as hydrated manganese dioxide; similarly, divalent lead ion is oxidized to quadrivalent lead ion, which precipitates out as hydrated lead dioxide; bismuth ion also behaves similarly. The formation of lead dioxide on the anode can be carried out quantitatively and may be used as the basis of a method for determining lead as explained in § 424.

397. Solution of the Anode. — With the foregoing illustrations of the oxidizing effect of the current at the anode, we may well ask why this effect does not extend further and cause the oxidation of some of the metal of the anode to the ionic form, thus,

$$Pt° \rightarrow Pt^{++++} + 4 e,$$
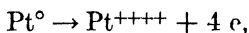
thereby bringing about a solution of the anode. The answer is that with the noble metals Pt, Åu, etc., it requires a very large anodic voltage to effect the transformation

$$M° \rightarrow M^{n+} + n e.$$
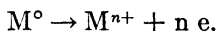
This means that potentials which will discharge hydroxyl ion are below the necessary value to effect the solution of platinum or gold. Though platinum is less noble than gold, it generally requires a higher potential to dissolve it; platinum does, however, dissolve slightly when used as an anode in sulfuric acid solutions; in hydrochloric acid or ammoniacal solutions, the solubility is greater.

[7] Knobel, Caplan and Eiseman, *Trans. Electrochem. Soc.*, **43**, 55 (1923).

If the solution contains platinum it is probable that some of it will deposit on the cathode. It has been shown [8] that platinum, which deposits during the deposition of copper, may remain attached to the cathode after the copper has been removed with nitric acid. Consequently, in the determination of copper, the weight of the platinum cathode should be obtained after the removal of the copper from the electrode, rather than before carrying out the electrolysis.

398. External Difference of Potential Required at End of Electrolysis. — If the electrolysis considered in § 393 is continued until simultaneous deposition of copper and hydrogen gas takes place, the external difference of potential, E, required is obtained from

$$E = (e_{O_2, OH^-} - e_{H^+, H_2}) + (\xi_{O_2} + \xi_{H_2}) + IR$$

where the quantity $(e_{H^+, H_2} - e_{O_2, OH^-})$ is the theoretical decomposition voltage of the cell, the quantity $(\xi_{O_2} + \xi_{H_2})$ is the overvoltage of the cell, and IR is the voltage required to overcome the resistance R of the solution in the cell.

On substituting the appropriate values for the electrolysis discussed in § 393, we have

$$E = 1.22 - (-0.01) + (1.16 + 0.58) + 0.8 \times 0.20 = 3.12 \text{ volts.}$$

399. Electrolytic Separation of Various Metals. — From a consideration of the preceding paragraphs it becomes apparent that the necessary condition for the electrolytic separation of one metal from another is that there be a sufficient difference between their deposition potentials so that one metal shall be quantitatively deposited before the deposition potential of the other shall be reached. The best way to show the various possibilities is to assemble the deposition potentials of the various metals in one chart. Such an assembly is shown in Figure 81 where the curves with the legends written above their horizontal portions represent the approximate deposition potentials of the given metals upon themselves for ionic concentrations from 0.02 M down to 10^{-8} M, while the curves with the legends written under their horizontal portions represent the approximate deposition

[8] T. L. Kelley and J. J. Molloy, *J. Am. Chem. Soc.*, **53**, 1337 (1931).

potentials of hydrogen upon the several metals with increasing current densities, the concentration of hydrogen ion being assumed to be 0.8 M. When from solutions of simple salts such as sulfate, nitrate, or chloride, we deposit Au, Pt, Ag, Hg, Cu, As, Bi, Sb, Sn, Pb, or Cd on themselves, from solutions which are not extremely dilute, by means of a current density not greater than 0.02 amp./cm.², the overvoltage is nil. For Ni, Co, Cr, or Fe under similar conditions, the overvoltage is about 0.15 volts.
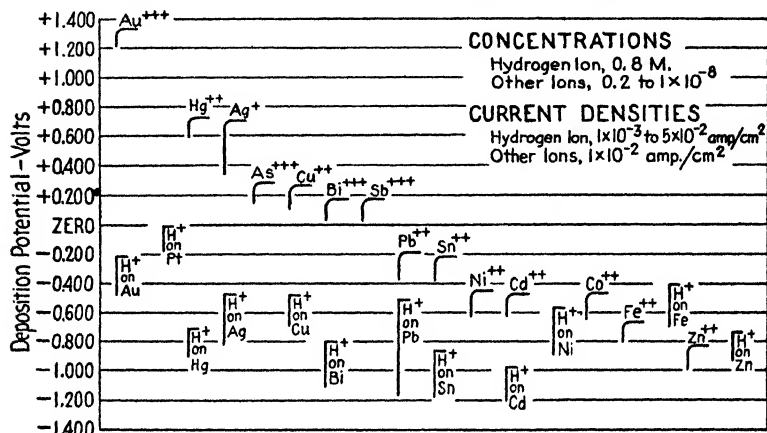
Fig. 81

Deposition Potentials of Metals on Themselves and Deposition Potentials
of Hydrogen on a Variety of Metals

When the metal ion concentration is very small the overvoltage of the metal may be considerable. In drawing the deposition potential curves of the metals in Figure 81, however, the overvoltage has been assumed to be nil throughout electrolysis except in the cases of Ni, Co, and Fe, for which an overvoltage of 0.15 volts has been assumed.

From the assembly of curves it is seen that gold can be separated from silver; silver from copper; copper from lead, tin, nickel, cobalt, iron, and zinc, but *not* from arsenic, bismuth, and antimony. Furthermore, if the problem is to plate out zinc from an acid solution, copper is a better cathode to use than platinum because the deposition voltage of hydrogen on platinum does

not fall low enough to give the value required for the deposition
of zinc.

400. Arbitrary Shifting of the Deposition Potentials of Metals.
— Since the deposition potential of a metal or non-metal is the
algebraic sum of the equilibrium potential and the overvoltage
potential, any alteration in either the equilibrium potential or
the overvoltage will affect the value of the deposition potential.
Methods of changing the equilibrium potential will be considered
in § 401 and methods of changing the overvoltage will be con-
sidered in § 402.

401. *Methods of Changing the Equilibrium Potential.* — The
equilibrium potential may be arbitrarily altered in any one of
three ways: first, by decreasing the ionic concentration of the
ion being discharged; second, by decreasing the concentration
of the metal in the deposited state; third, by changing the
temperature.

The scheme of decreasing the ionic concentration is most readily
brought about by tying the ion up in the form of a complex having
a small instability constant. Often cyanide or tartrate ion is
added for this purpose. Thus, for the instability constant of
the cuprocyanide ion $Cu(CN)_3^-$ we have

$$\frac{[Cu^+][CN^-]^3}{[Cu(CN)_3^-]} = 0.5 \times 10^{-27}.$$

In a solution of 0.1 M potassium cuprocyanide containing 0.01
M excess of potassium cyanide, the concentration of cuprous ion
will be equal to 5×10^{-23}. The equilibrium potential between
the cuprous ion and metallic copper will be

$$e = 0.059 \log \frac{5 \times 10^{-23}}{1 \times 10^{-13 \cdot 5}} = -0.52 \text{ volts,}$$

whereas in a 0.1 M copper sulfate solution the equilibrium potential
between the cupric ion and metallic copper is $+0.23$ volts. The
effect of forming the complex has therefore been to decrease the
equilibrium potential by 0.75 volts.

The scheme of decreasing the concentration of the metal in the
deposited state is effected by employing mercury as the cathode,
the deposited metal dissolving in the mercury and forming an

amalgam. For the equilibrium potential between an ion and its metal when the latter is dissolved in mercury, we are led to expect, on the basis of Nernst's formula, that the potential is a function not only of the concentration of the ion but also of the concentration of the dissolved metal, and this expectation is verified by experiment. Thus, in a solution of 1.0 M sodium chloride at 18°, Le Blanc [9] found the following equilibrium potentials between the sodium ion and different sodium amalgams of the compositions given: .

Composition of Amalgam	Equilibrium Potential $Na^+ \rightleftarrows NaHg$
0.5% Na	−1.308
1.0% Na	−1.323
2.0% Na	−1.358

The equilibrium potential between sodium ion at the same concentration and pure metallic sodium has the value of −2.748 volts, theoretically calculated for the same temperature of 18°.

The scheme of altering the temperature results in positive potentials becoming more positive when the temperature is increased and less positive when the temperature is lowered. Likewise, negative potentials are made more negative by an increase in temperature and less negative by a lowering of the temperature. These results are in accordance with Nernst's equation,

$$e = \frac{0.0001983\ T}{n} \log \frac{[\text{Ion}]}{K}.$$

402. Methods of Changing the Overvoltage. — The overvoltage may be arbitrarily altered in any one of several ways (§ 392), namely; by selecting a different kind of metal for the electrode, by changing the physical condition of its surface, by changing the ionic concentration of the element being deposited, by changing the current density, or by changing the temperature.

The scheme of selecting a different kind of metal for the electrode or of changing the physical condition of the metal surface is not

[9] *Z. physik. Chem.* **5,** 473 (1890).

of very wide avail, so far as the usual conditions of analytical procedure are concerned, because the analyst must use as a cathode a metal which has a very slight tendency to go into solution, such as platinum, gold, or silver, and a cathode of any of these metals on which an appreciable layer of some other metal has been deposited will behave just as though it were composed completely of the metal being deposited.

The scheme of altering the ionic concentration of the element being deposited rests upon the fact that the smaller the ionic concentration, the greater the overvoltage for a given current density. Hence, if a metal is deposited from a solution where its ion is tied up in the form of a complex (cyanide, tartrate, etc.) so that its ionic concentration is extremely small, the deposition will be attended with considerable overvoltage. Thus the deposition of copper from the 0.1 M potassium cupro-cyanide solution, mentioned in § 401 and containing a concentration of cuprous ion equal to 5×10^{-23}, is attended with an overvoltage effect of 0.510 volts when a current density of 0.003 amp./cm.^{2} is used, whereas the overvoltage effect for the deposition of copper from a 0.1 M copper sulfate solution is only 0.020 volts for a similar current density.

The changing of the current density is the most available scheme that the analyst has for changing the overvoltage. For the deposition of metal on metal, the change in the overvoltage due to change in current density is relatively small, but for the deposition of hydrogen on metal, the change in overvoltage due to change in current density is very great, as shown by the figures obtained by Knobel, Caplan and Eiseman, given in Table 58.

403. Character of Cathodic Deposits and Relation to Current Density. — What is desired for analytical purposes is a deposit that is coherent, dense, smooth and glistening; what is not desired is one that is flaky, spongy, powdery, granular or rough. A cathodically deposited metal is essentially crystalline, although it often takes considerable magnification (up to 200 diameters) to reveal this fact. Now it is found by experiment that an increase of current density up to a certain critical current density does lead to a diminution of the grain size in a metallic deposit. At current densities above this critical value, which varies ac-

cording to the nature of the electrolyte, the thoroughness with which it is kept mixed, the temperature, and other factors, local depletion of ionic concentration will occur at the surface of the cathode and tend to favor the growth of the deposit at certain points, thereby producing excrescences. Such phenomena will occur most readily if the ionic concentration is low or if the circulation is inefficient. Finally, if the current density is raised sufficiently, hydrogen ion discharge will become possible, owing to depletion of metal ions near the cathode. If an appreciable evolution of hydrogen gas occurs, the deposit will become broken up and irregular. Porous, spongy, and incoherent deposits are generally obtained under such conditions. This effect will occur most easily with the baser metals, but, in any case, will be favored by low metal ion concentration, high hydrogen ion concentration, and insufficient stirring.

For analytical purposes, the current densities that are employed are seldom in excess of 0.1 amp./cm.^{2} and usually about 0.01 amp./cm.^{2}

The theory of the mechanism of electrolytic deposition is explained by Allmand and Ellingham [10] as follows: In the deposition of metals from solutions containing their simple ions at reasonable concentrations, the electrochemical process is merely the discharge of these ions to give free metal atoms. The atoms then arrange themselves so as to produce the aggregation of crystals of which the deposit consists. This crystallization process may be compared with that which occurs in the separation of a sparingly soluble substance as a precipitate from a solution in which it has just been formed. In this latter case, the more highly supersaturated with the substance the solution is, the more finely divided is the precipitate formed. In cathodic metal deposition, a high rate of discharge of metal ions will mean a considerable saturation with regard to metal atoms at the cathode surface and hence a fine-grained deposit. If, however, the conditions are such that the degree of supersaturation is relatively small, the tendency will be for existing crystals to grow rather than for new crystal nuclei to form, and the deposit will consist of a comparatively small number of well-developed crystals.

[10] On p. 121 of reference cited in § 392.

404. Time Required in Electrolysis. — The time necessary for the quantitative deposition of a metal would be an easy matter of calculation if the deposition of the metal ion alone accounted for all the current used during the electrolysis, because then, in accordance with Faraday's Law, the quantities of metal, given in Table 61, would be deposited by a current of one ampere in the times mentioned:

Table 61

ELECTROCHEMICAL EQUIVALENTS

Metal	Milligrams Deposited by 1 Ampere	
	Per Minute	Per Hour
Gold..................	40.9	2452
Platinum..............	30.3	1820
Silver.................	67.1	4025
Mercury..............	124.6	7477
Copper...............	19.7	1185
Arsenic...............	15.5	932
Bismuth..............	43.1	2585
Antimony............	24.9	1495
Tin..................	36.9	2219
Nickel................	18.2	1094
Cobalt...............	18.3	1099
Cadmium.............	34.9	2096
Zinc.................	20.3	1219

In point of fact, however, as the electrolysis progresses, a smaller and smaller fraction of the current is accounted for by the deposition of the metal, or, in other words, a smaller and smaller weight of metal is being deposited in each succeeding unit of time until finally a state of equilibrium is reached when no further metal is deposited other than hydrogen. The effect of this is to lengthen the time required for the deposition considerably beyond that calculated on the assumption that there is a uniformly direct proportion between the rate of deposition of the metal and the current strength. Thus, for the electrolysis of a quantity of copper of 0.200–0.300 mg. with a current of 2 amp.,

it usually takes from two to three hours to remove the copper quantitatively, whereas, if we calculate the time on the assumption that 19.7 mg. of copper are being deposited per minute per ampere, the time would be only five to eight minutes. With efficient stirring to prevent local depletion of the electrolyte at the cathode, and with current strengths of 2–3 amp., most electrolyses can be performed in two to three hours for amounts of metals up to 300 mg.; with smaller current strengths, proportionally longer times will be required.

405. Anodic Deposition. — The electrolysis of solutions containing lead, antimony, manganese, bismuth, tin, or silver may result in the deposition of oxides of these metals on the anode. In the case of lead, quantitative deposition of the metal as PbO_2 can be effected under the proper conditions in the presence of nitric acid and may be used as the basis of a method for the determination of lead. The reaction involved is

$$Pb^{++} + 2\ OH^- \rightarrow PbO_2 + 2\ H^+ + 2\ e.$$
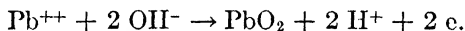
The solution should have a hydrogen ion concentration of 1.5 M or more in order to prevent deposition of lead on the cathode. A platinum gauze anode and a platinum wire cathode should be used.

To obtain an adherent deposit, an initial current density of 0.01 amp./cm.^{2} is advisable, followed by a gradual increase to above 0.015 amp./cm.^{2} When the addition of sulfate ion will not interfere with subsequent determinations, the adherence of the deposit may be increased by adding 1 ml. of 18 M sulfuric acid. The details of this method are given in § 424 in connection with its use in the analysis of brass.

406. Source of Current and Regulation of Voltage. — For the usual set-up of apparatus [11] and for the general run of electrolytes that are employed by the analyst, it is seldom that a voltage less

[11] We have in mind an electrolytic beaker of 6–7 cm. diameter and 9–11 cm. height; an anode of platinum wire of 1 mm. thickness and bent into the form of a cylindrical spiral of several turns of 2–3 cm. diameter, the spiral being immersed in the electrolyte to the depth of three or four of its turns and being centered with respect to the central axis of the beaker; and a plate or gauze electrode of platinum about 10 cm. wide by 10 cm. deep.

than two volts or greater than five volts will be required as measured across the electrodes. To provide such a voltage one can use a bank of wet cells or storage batteries arranged in series, or one can use the house current after suitable reduction of its voltage, provided it is direct. If it is an alternating current, it must be rectified and reduced to a suitable voltage. *In any event, no electrolysis should ever be attempted unless the electrolytic circuit is provided with an ammeter in series with the current and a voltmeter shunted across the electrodes.* The objection to the use of wet cells or storage batteries is that they can deliver only a limited number of ampere hours before becoming exhausted; hence, one must always have enough knowledge of their previous use to be sure that there is still a sufficient number of ampere hours for the work in hand. With this exception, the use of wet cells or storage batteries is quite satisfactory. The use of dry cells is not suited to continuous service.

As shown in physics, the voltage of a bank of batteries when the latter are placed in series is equal to the sum of the voltages of the individual batteries. The voltages of the common batteries on the market are given herewith:

Primary Cells (wet)	*Initial Voltage*
Chromic Acid ($K_2Cr_2O_7 - H_2SO_4 - Zn$)	2.0
Daniell ($Zn - Cu$)	1.08
Edison Primary ($CuO - Zn$)	0.95
Storage Batteries	
Edison Storage ($NiO - Fe - KOH$)	1.70
Lead-Acid ($PbO_2 - PbSO_4 - H_2SO_4$)	2.00

The use of the house current is very convenient provided the current is a direct current, but it offers the disadvantage that the voltage must be very greatly reduced before the current can be used, because the ordinary service voltage is 110–125 volts, whereas the voltage that is needed is 2–5 volts. In speaking of the methods by which we may reduce the voltage, we shall, by way of warning, first describe an improper method which always seems to suggest itself readily enough but yet does not make apparent the danger to which it exposes the operator.

407. *Improper Method of Wiring.* — The improper method is to place a resistance in series with the electrolyte as indicated in Figure 82.   Suppose the service voltage is 110 volts and the voltage across the electrodes of the electrolyte is 3 volts; for a current of 2 amp., the value of the resistance R that must be used is $\dfrac{110-3}{2}$ = 53.5 ohms.   Now suppose the deposition to be at an end, the electrolyte to have been replaced with water preparatory to disconnecting and removing the cathode, the current still being

Fig. 82

Improper Electrolytic Circuit

allowed to flow, however, in accordance with the rule that is always followed that the current shall be turned off only after the cathode has been taken out of the circuit.   Under these conditions, the voltage across the electrodes, instead of being 3 volts, is 109 volts, so that if the operator attempts to remove the cathode with his fingers, he may get a very serious shock. . To show that the voltage across the electrodes is 109 volts, it is only necessary to show what the resistance between the electrodes is, because the voltage drop along any portion of a circuit is proportional to the resistance of that portion.   For pure water, the specific resistance is 10^6 ohms/cm.^{3}, so that the resistance between the electrodes becomes

$$\frac{10^5 \times 6}{10^2} = 6{,}000 \text{ ohms,}$$

whence the voltage x across the electrode is obtained from $(53.5 + 6{,}000) : 6{,}000 :: 110 : x$, which upon solving gives $x = 109$ volts, approximately.

It should be pointed out that the strongest current that a person can receive through his fingers, up his arms and across his chest and still be able to release his grip, is 5 milliamperes, and that currents of this or greater magnitude are physiologically dangerous.   Now the resistance of the human body through the parts named may be as low as 1,000 ohms in some persons; consequently, to grasp the

cathode when the voltage between it and the anode is 109 volts means that the operator is liable to a body current of 100 milli-amperes if he touches some other part of the circuit at the same time. *The largest voltage across the electrodes that it is at all safe to deal with is 5 volts.*

408. Proper Method of Wiring. — The proper method of wiring is to place a resistance in series with a smaller variable resistance and to connect the electrolyte in *parallel* with the latter as indicated in Figure 83.

To show how this arrangement works, let E' be the voltage drop through the variable resistance r_3; this drop will be the same as that which exists across the elec-

Fig. 83

Proper Electrolytic Circuit

trodes of the electrolyte because of the parallel combination. Now the value of E' is determined by the ratio of the total resistance of the circuit to the resistance of the parallel portion, according to the proportion:

$$(R_1 + R) : R :: V : E' \qquad (1)$$

where R represents the resistance of the parallel portion of the circuit and V the service voltage. Our next step is to show how R depends on r_2 and r_3. To do this, let E'' be the counter e.m.f. of the electrolyte; then by application of the generalized form of Ohm's Law to the parallel portion, we have

$$\frac{E'}{R} = \frac{E' - E''}{r_2} + \frac{E'}{r_3}, \qquad (2)$$

or dividing through by E' and solving for R, we get

$$R = \frac{r_2 r_3}{r_2 + \left(\dfrac{E' - E''}{E'}\right) r_3}. \qquad (3)$$

Now if the value of R is such that E' is just equal to E'', no current can flow through the electrolyte, although it will flow through

the resistance r_3; hence, for such a condition $R = r_3$. If the value of R is such that E' is greater than E'', current will flow through the electrolyte; for such a condition the quantity in parenthesis in the denominator of (3) will always have a positive fractional value, and as r_3 is always positive, it follows that the denominator of (3) will always be greater than r_2. Hence R will always be less than r_3 for such a condition. Thus, in any event, the equivalent resistance R can never be greater than r_3, and, accordingly, the voltage drop through the variable resistance or across the electrodes can never be greater than the value of b found by solving the proportion,

$$(R_1 + r_3) : r_3 :: V : b. \qquad (4)$$

Thus, if the service voltage V is 110 volts, R_1 50 ohms, and r_3 is set at some definite value, say 2 ohms, it means that, no matter what the resistance of the electrolyte may be, the voltage drop across the electrodes cannot be greater than 4.25 volts in accordance with the proportion $(50 + 2) : 2 :: 110 : b$. The actual drop would be somewhat less than 4.25 volts and could easily be computed from equations (3) and (1) if the value of r_2 and the counter e.m.f., E'', were known.

409. Practical Set-up. — Because of the different values of r_2 that are encountered by virtue of different types of vessels, electrodes, etc., that are in use, it is advisable in the set-up to provide a certain flexibility in R_1 and r_3. With respect to R_1 the simplest thing is to construct a lamp-board [12] having four or five sockets in parallel, then by screwing in a successive number of lamps we cut down the resistance according to the rule for a parallel combination, *i.e.*,

$$\frac{1}{R} = \frac{1}{r'} + \frac{1}{r''} + \frac{1}{r'''} + \frac{1}{r''''} + \cdots$$

where R represents the equivalent resistance of the parallel combination, and r', r'', r''', etc., represent the individual resistances which make up the parallel combination. Thus, using lamps of

[12] Hard asbestos board, having a thickness of about ¼ inch, serves as an excellent material from which to make the lamp-board.

60 watts-110 volts, the corresponding equivalent resistances of the combination would be as follows:[13]

Number of lamps	1	2	3	4	5
Equivalent resistance (ohms)	200	100	67	50	38

With respect to r_3, the simplest thing is to use a rheostat with a maximum resistance of 10 ohms and maximum carrying capacity of 5 amp. In addition to the foregoing equipment, a voltmeter
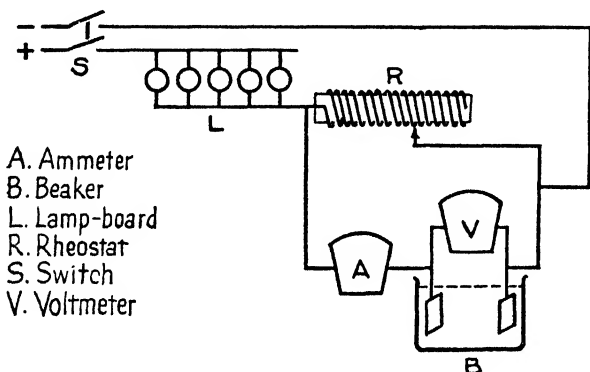

A. Ammeter
B. Beaker
L. Lamp-board
R. Rheostat
S. Switch
V. Voltmeter

Fig. 84

Diagram of Electrolytic Circuit for Using House Service

with a range of 0–10 volts and an ammeter with a range of 0–5 amp. are indispensable. The plan of the entire circuit is portrayed in Figure 84. Stands for supporting the electrodes are not represented in the diagram. The stands should preferably have a column of glass or of some other nonconducting material because then they can be touched while the current is flowing. The size of wiring to be used for the lamp-board and for other parts of the circuit should be in accordance with the values given in Table 62.

[13] To figure the resistance of a lamp from its specification in terms of watts and volts, divide the square of the number of volts by the number of watts; thus for a lamp of 60 watts-110 volts, we have for its resistance $\dfrac{110 \times 110}{60} =$ 200 ohms (approx.).

Table 62

CURRENT-CARRYING CAPACITY OF COPPER WIRE

Size of Wire		Current Carrying Capacity Rubber Insulated Copper Wire
B & S Gauge	Thickness, Inches	Amperes per Conductor
18	0.0403	3
16	0.0508	5

410. Stirring. — It is all important in any electrolytic deter-mination to prevent local depletion of the electrolyte at the sur-face of the cathode. Consequently, a great many different schemes have been used to effect this end; among such schemes may be mentioned the rotating anode,[14] the rotating cathode,[15] the use of a magnetic field,[16] etc. The various schemes, however, differ mostly in mechanism and not in principle as they are all based on the main idea of thorough and efficient stirring. There is, therefore, not much advantage of one scheme of stirring over another if both cause a thorough circulation of the electrolyte. One of the easiest ways to accomplish this desired result is by means of a small glass propeller which is driven by means of a motor. The glass propeller is easily made by flattening out the end of a stout stirring rod (6 mm. diameter) into a small oval blade, say 10 mm. × 8 mm., and then turning the blade so that one of its axes lies in a plane which is perpendicular to the stirring rod and the other axis cuts the plane at a slight angle. For use, the propeller should be placed well below the level of the electrolyte and the beaker centered with respect to the stirring rod which forms the shaft of the propeller. The free end of the stirring rod should be rigidly connected to a driving shaft by means of an adjustable jaw. The speed at which the propeller should run is 500–700 revolutions per minute. See Figure 85, § 414.

[14] F. F. Exner, *J. Am. Chem. Soc.*, **25**, 896 (1903).
[15] F. A. Gooch and H. E. Medway, *Am. J. Sci.* (4) **15**, 320 (1903).
[16] G. L. Heath, *Ind. Eng. Chem.*, **3**, 76 (1911).

411. Cathodes. — Generally speaking, cathodes should be of platinum. It is found that gauze cathodes give much better deposits than plate cathodes. The reason for this seems to be that the interstices in the gauze bring about a much better circulation of the electrolyte so far as conditions at the surface of the electrode are concerned, the better circulation serving to keep down any local depletion of the electrolyte that might tend to occur.

To obtain the active area of a 52 mesh gauze cathode made from wire having a diameter of 0.004 inches, and that of a 45 mesh cathode made from wire having a diameter of 0.0078 inches, 22 per cent and 96 per cent should be added respectively to the areas obtained by multiplying the width of the gauze by its height.

412. Examples.

1. Calculate the theoretical decomposition potential, at 25°, of a solution which is 0.1 M with respect to cupric ion and molar with respect to hydrogen ion.

2. In the electrolysis at 25° of a 0.001 M solution of cupric ion, which is molar with respect to hydrogen ion, platinum electrodes were used and a cathodic current density of 0.005 amperes/cm². Assume the anodic overvoltage to be 1.10 volts. The area of the cathode is 81.0 cm.², and the resistance of the solution in the cell is 0.101 ohms. The overvoltage of copper is nil. Calculate the voltage required at the beginning of the electrolysis to deposit appreciable quantities of copper and oxygen. If the electrolysis is continued until hydrogen gas is evolved at the cathode, what must be the applied voltage? Assume a constant hydrogen ion concentration throughout the electrolysis.

3. In an electrolytic determination, the anode was a platinum wire 15 inches long having a diameter of 0.064 inches. A 52 mesh cylindrical cathode made of wire 0.004 inches in diameter two inches high and one inch in diameter was used. A current of 2.5 amperes was employed. Calculate the approximate anodic and cathodic current densities.

4. Assuming an overvoltage of silver ion on a silver cathode of 0.02 volts, calculate the deposition potential at 25° of silver from a solution which is 0.003 M with respect to silver ion.

5. A solution containing silver ion is 0.02 M with respect to cupric ion. Silver is electrodeposited from this solution at 25° until 100 ml. of the solution contains 10.8×10^{-4} g. of silver. Will copper be co-deposited?

CHAPTER XX

ELECTROLYTIC DETERMINATION OF COPPER

413. General Considerations. — In the electrolytic method of determining copper, the sample is dissolved to form a solution containing the cupric ion. This solution is then electrolyzed under conditions which bring about, as completely as possible, the deposition of copper on the cathode and, at the same time, minimize as much as possible the effects of interfering elements. The cathode and the deposit are weighed, after which the deposit is dissolved and the cathode alone is weighed. The difference between these weights is the weight of the deposit. If only copper has been deposited and its deposition has been quantitative, the per cent of copper in the sample can readily be calculated from the weight of the deposit and the weight of the sample. When appreciable copper remains undeposited, it must be determined by some suitable method and a correction applied. When bismuth is present, it may co-deposit with the copper, in which case the deposit must be analyzed for bismuth and a correction applied.

414. Practical Points in the Determination of Copper. — It is assumed that the student is familiar with the general theory of electrolytic determinations (Chapter XIX), and is familiar with the special apparatus which is required for this kind of work, namely, platinum electrodes, electrode stands (preferably of nonconducting material), a stirring device, a suitable electrical set-up for safely employing and regulating the current, an electrolytic beaker, and a pair of split watch-glasses.

With respect to the electrodes, the anode usually consists of a platinum wire having a thickness of about 1 mm. and bent into the form of a spiral; the cathode should preferably be in the form of a rectangular piece of wire mesh about 8 cm. wide × 7 cm. deep, the mesh being composed of wires which have a diameter about 0.1 mm. and which are spaced about 0.5 mm. between

centers. If wire mesh is not available, a thin rectangular plate about 8 cm. wide × 7 cm. deep × 0.1 mm. thick will answer the purpose. Whichever electrode is used, the gauze or the plate, it should be bent to correspond to the curvature of the electrolytic beaker. Some analysts use a large platinum evaporating dish of about 100–150 ml. capacity, making the dish serve the double purpose of containing the electrolyte and acting as the cathode at the same time. Before being used, both the anode and cathode should always be immersed in hot 6 M nitric acid for a few moments, then thoroughly rinsed with distilled water, and finally ignited to a bright red over the colorless flame of a Bunsen or Meker burner. By this treatment, any grease or other impurity that might contaminate the electrode is removed and a fresh, clean surface produced; this cleanliness of electrode surface, particularly with respect to the cathode, is very necessary for securing a satisfactory deposit. After being cleaned, the anode

Fig. 85

Detailed Assembly for Electrolytic Determinations

and cathode are used at once, the latter without being weighed. The reason for not weighing the cathode beforehand is found in the fact that the anode dissolves slightly during the electrolysis (§ 397) to the extent of several tenths of a milligram and this dissolved platinum is plated out on the cathode. Consequently, the cathode is not weighed until the electrolysis is completed; it is then weighed with its deposited copper, after which the copper is dissolved off by means of 6 M nitric acid, and the cathode itself weighed, all according to the directions given in § 416. With respect to electrode stands, nothing special need be said except that they be made preferably of a nonconducting material and that they be provided with a firm base and an adjustable binding post (see Figure 85).

In regard to a stirring device, we have already mentioned the several types in § 410 and have described there in detail the device which we regard as the simplest, namely, the motor-driven glass propeller.   Some one of these devices is absolutely necessary where cathodic current densities of 0.01 to 0.02 amps./cm.² (so-called "rapid" methods of deposition) are to be used, such current densities usually effecting a quantitative deposition in two hours or less; if cathodic current densities of 0.001 to 0.002 amps./cm.² (so-called "slow" methods of deposition), which require twelve to fifteen hours, are to be used, stirring may be omitted.

In regard to the electrical set-up for adapting the house service to electrolytic determinations, although we have already gone into this matter in §§ 406–409, the matter of using only the proper kind of set-up is so important that we advise a perusal of these paragraphs again, especially where a procedure requires, as some procedures do, that, before detaching the cathode, the electrolyte should be replaced by water with simultaneous washing of the cathode while the current is still kept flowing, or, as other procedures require, that the cathode should be gradually lifted out of the electrolyte while the current is still flowing.

With respect to the beakers used for electrolytic purposes, these differ from ordinary beakers only in the fact that they possess two lips instead of one; the two lips are placed opposite each other and are rather deeply recessed so as to accommodate the anode and cathode stems in a satisfactory manner.   Split watch-glasses are necessary to catch the spray which is occasioned by the oxygen and hydrogen gases that are evolved at the anode and cathode, respectively; . the glasses should be bored at their center so that the propeller shaft can pass through them (see Figure 85).

415. Interfering Elements in the Determination of Copper in an Ore. — The interfering elements that are likely to be encountered in a copper ore are gold, silver, lead, arsenic, antimony, selenium, bismuth, iron, nickel, cobalt, manganese, and zinc.   Of these elements, the following are deposited at potentials which apply to the deposition of copper, namely, gold, silver, arsenic, antimony, selenium, and bismuth.   Lead and manganese are not

deposited as metals, but appear at the anode as lead peroxide and manganese dioxide, however, and, if they are present to the extent of more than several milligrams, the oxides are likely to become detached from the anode and become entrained in the deposit being formed at the cathode. Iron does not deposit, but, if much of it is present, it arrests the deposition of the copper in the last stages by virtue of the fact that the ferric ion resulting from the oxidizing action at the anode is reduced at the cathode in preference to the cupric ion; or, stated another way, the presence of much iron keeps the deposition potential at the cathode at such a value that copper cannot be quantitatively precipitated. Nickel, cobalt, and zinc will not deposit if the solution has a concentration of hydrogen ion greater than 0.2 M, so that, when such concentrations of hydrogen ion are employed in the electrolysis, as is usually the case, these elements will not interfere. When the deposition of the copper is made from an alkaline solution, these metals will also deposit.

Treatment of Interfering Elements.— The following is the general scheme for taking care of interfering elements. If the percentage of arsenic is appreciable, the portion which is weighed out for analysis, before being dissolved, is ignited just to dull redness in an open porcelain crucible with full access of air for about 30 minutes. In order to avoid slagging of the copper ore with the porcelain crucible, care must be taken not to employ too high a temperature. This ignition will volatilize most of the arsenic and selenium. After this preliminary ignition, or without it, if the content of arsenic is small, the sample is dissolved by a mixture of nitric, hydrochloric and sulfuric acids. The solution is evaporated to fumes of sulfur trioxide and is then digested with a small amount of water. By this treatment, most of the selenium will be precipitated as the metal; the lead, except for a few milligrams, will be precipitated as sulfate; the silver will be precipitated as silver chloride, unless the fuming is conducted long enough to transpose the chloride to the more soluble sulfate. If this should take place, silver should be precipitated as chloride and removed by filtration, after which a little sulfuric acid is added and the solution is again heated until fumes of sulfur trioxide are evolved. Most ores are completely decomposed by the above

treatment; certain silicates, slags, etc., however, require fusion of the residue. For the procedure in such cases, see § 416. After the acid treatment, sufficient water is added to dissolve soluble salts. Then the insoluble residue is removed by filtration. The solution is neutralized with ammonium hydroxide and sufficient hydrochloric acid added to make it 0.3 M with respect to hydrogen ion. The solution is then saturated with hydrogen sulfide to precipitate the copper as sulfide. This precipitate may contain sulfides of bismuth, antimony, arsenic, etc., together with small amounts of co-precipitated sulfides of zinc, iron, etc. The precipitate is removed by filtration; the filtrate being discarded if only copper is to be determined and retained if some metal besides copper is to be determined. The filter paper and precipitate are placed in a flask, 40 ml. of 16 M nitric acid is added and the solution is boiled gently to dissolve the precipitate and filter paper. The solution is diluted, filtered and neutralized with ammonium hydroxide, and then made acid with a definite concentration of nitric acid. After being diluted with water to the desired acidity, the solution is titrated with 0.02 M KMnO$_4$ to oxidize arsenic and antimony to the pentavalent state and thereby to make the deposition of these elements more difficult. 10 ml. of 3% hydrogen peroxide is then added and the solution is electrolyzed. During electrolysis, more hydrogen peroxide is added from a burette at the rate of 5 drops per minute. While the electrolysis is in progress, nitrous acid tends to form at the cathode thus:

$$2 \, e + 3 \, H^+ + NO_3^- \rightarrow HNO_2 + H_2O.$$
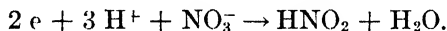
The nitrous acid formed accelerates the dissolving of copper from the cathode[1] and prevents quantitative deposition of copper. The hydrogen peroxide[2] added before and during electrolysis prevents accumulation in the solution of nitrous acid. The addition of hydrogen peroxide also tends to keep the arsenic and antimony in the pentavalent state throughout the electrolysis and thus to prevent their deposition. When bismuth is present, BiO$_2$ may deposit at the anode, become detached and subsequently contaminate the cathode. The addition of hydrogen

[1] Veley, *Proc. Roy. Soc.*, **46**, 216 (1889).
[2] J. W. Stillman, Dissertation, Columbia University, 1920.

peroxide will prevent anodic deposition of BiO_2 and thus avoid error from this source. Often the hydrogen peroxide solution has a concentration far less than the manufacturer's label indicates, so that before use its concentration should be determined by titration with $KMnO_4$ solution.

During electrolysis, bismuth, if present, will be in the form of bismuth ion and while this ion is not quantitatively deposited at the cathode, since some of it is invariably oxidized to the peroxide at the anode, still, a very appreciable amount of it will always be deposited with the copper, often without causing any perceptible discoloration of the deposit. No attempt is made to remove bismuth ion beforehand; it is allowed to co-deposit with the copper and then the amount of bismuth in the copper deposit is determined separately as described in § 416.

Treatment of Undeposited Copper.— After the electrolysis has been completed, and the cathode, with its deposit, has been removed, the solution should be saturated with hydrogen sulfide to precipitate, as copper sulfide, any copper which did not deposit. The filtrate and washings should be saved if metals besides copper are to be determined. The undeposited copper may often amount to several milligrams. The precipitate of copper sulfide is washed on the filter paper with 3 *M* colorless ammonium sulfide to wash out any arsenic and antimony sulfides; it is then dissolved in nitric acid. The solution is made alkaline with ammonium hydroxide, a few milliliters of 3 *M* ammonium carbonate is added and the solution is boiled for a few minutes. If basic bismuth carbonate forms, it is filtered off on filter paper. The filtrate is made acid with hydrochloric acid and saturated with hydrogen sulfide; after being allowed to settle, the precipitated copper sulfide is filtered off on a weighed porcelain Gooch crucible, ignited to CuO and weighed as such.

416. Exercise No. 48. Determination of Copper in a Copper Ore. — Weigh from 0.5 to 1.0 g. of the finely ground ore, igniting it in a porcelain crucible if the ore contains much arsenic (§ 415), and transfer to a covered casserole. Add about 20 ml. of 16 *M* nitric acid, 5 ml. of 12 *M* hydrochloric acid, and 5 ml. of 18 *M* sulfuric acid. Heat the casserole and its contents until decomposition of the ore is complete, remove the cover of the casserole,

and evaporate the solution to dense fumes of sulfur trioxide. Cool, add carefully about 40 ml. of water and heat to dissolve soluble salts. Filter through a small filter paper and wash with hot water. Most ores are completely decomposed by this treatment. Certain silicates, slags, etc., however, require fusion of the residue from the acid treatment. In case fusion is necessary, remove beforehand any lead sulfate which may be present in the residue, by means of repeated extraction with hot 3 M sodium acetate solution. Remove silver chloride, if present, by repeated treatment of the residue with hot 6 M ammonium hydroxide solution. Fuse the residue, which has been freed of lead and silver salts, with sodium carbonate and decompose the fused mass with hydrochloric acid in the manner described in § 230. Add sulfuric acid to the solution and evaporate to fumes of sulfur trioxide. Dissolve the soluble salts in water, filter, and add the filtrate and washings to the main solution.

If silver is present in the main filtrate, due to too long fuming with sulfuric acid, it must be removed by precipitation as chloride, followed by filtration and evaporation of the filtrate to fumes of sulfur trioxide after addition of a few milliliters of 18 M sulfuric acid as directed above.

Bring the solution to a volume of about 100 ml. and neutralize it to litmus paper by the cautious addition of 15 M ammonium hydroxide solution; add sufficient 6 M HCl to make the solution 0.3 M with respect to hydrogen ion and saturate with hydrogen sulfide. Filter and retain the filtrate, if any metal besides copper is to be determined. When filtration is complete, place the filter paper containing the precipitate in an Erlenmeyer flask and add 40 ml. of 16 M HNO$_3$. Apply heat and disintegrate the filter paper by means of a stirring rod. When the precipitate and filter paper are completely dissolved, dilute with water to about 85 ml. and then cautiously neutralize the contents of the flask with a solution of 8 M NH$_4$OH. Now make the solution acid by adding 20 ml. of 8 M HNO$_3$.

If arsenic or antimony is present, titrate the solution to a pink color with 0.02 M potassium permanganate in order to oxidize both arsenic and antimony to the pentavalent state. Dilute the solution to 200 ml. with distilled water. If arsenic and

antimony are absent, the titration with potassium permanganate should be omitted.   Now add 10 ml. of 3% H_2O_2 to the solution.

Adjust a clean, ignited, but unweighed platinum cathode in the beaker, dilute the solution if necessary so that it completely covers the cathode, and connect the latter to the negative terminal of the source of current.   Suspend the anode in such a manner that it is about equally distant from all parts of the cathode; see that it does not foul any part of the stirring device, and then connect it to the positive terminal of the source of current.   Cover the beaker with split watch-glasses.   Start the stirring device and pass through the solution a current of 0.01–0.02 amp./cm.^{2} of cathode area, and set the variable resistance (consult § 409 for the correct wiring diagram) so that the voltage drop across the electrodes shall be 2.5–3.0 volts.   Continue the deposition of copper for two hours and a half.   During electrolysis add from a burette a 3% solution of hydrogen peroxide at the rate of 5 drops per minute.   When it appears that all the copper has been plated out, raise the level of electrolyte slightly by adding 20–25 ml. of water so as to expose a fresh portion of cathode stem, and see whether any more copper plates out in 15 minutes; if it does, continue the electrolysis for 30 minutes longer and repeat the test; when no further copper plates out, the electrolysis may be considered to be finished, although, as already stated, it is generally the case that several milligrams of copper still remain in the solution, *and must be recovered* as directed in § 415.   When the electrolysis is considered finished and while the current is still flowing, gradually lower the beaker until the cathode is completely out of the electrolyte, meanwhile washing the cathode with distilled water.   As soon as the cathode is entirely out of the electrolyte, turn off the current, wash the cathode with a little more distilled water, then with some 95% alcohol, and next place it in an oven at $105°–110°$ to dry for 2 or 3 minutes, but no longer, as otherwise the copper will oxidize; transfer to a desiccator and allow to cool.   If the deposit of copper is of bright, metallic luster and is firmly plated upon the cathode, it is ready for weighing; this weighing should be done at once since copper is subject to oxidation even at room temperature.

After weighing the cathode with the copper deposit, place the

cathode in a small beaker and dissolve the deposit by adding about 15 ml. of 8 M nitric acid. Wash the electrode with distilled water, then with a little 95% alcohol, and dry at 105°–110° for 2 or 3 minutes. Cool in a desiccator and weigh. Subtract this weight from the weight of the cathode with the Cu deposit; the difference will be the weight of Cu plus the Bi deposited.

Bismuth, if originally present in the ore, will have been deposited in part with the copper as mentioned in § 415, and must be determined in the solution obtained by dissolving the deposit from the cathode in nitric acid. To determine the weight of bismuth deposited, add cautiously an excess of ammonium hydroxide to the solution and then a few milliliters of 3 M ammonium carbonate solution and boil for a few minutes. Wash the precipitate of basic bismuth carbonate, which will probably be contaminated with a little copper, with hot water and 0.1 M ammonium hydroxide solution, and then dissolve in 3 M nitric acid. Reprecipitate with ammonium hydroxide and ammonium carbonate as before, filter, wash, and ignite in a porcelain crucible and weigh as Bi_2O_3. Calculate the weight of Bi and deduct it from the weight of deposit, to obtain the weight of Cu.

417. Electrolytic Determination of Copper in Alloys. — The electrolytic method of determining copper finds wide use in the analysis of alloys containing copper, such as German silver and brass. The details for the determination of copper in brass are given in §§ 424 and 425 and those for the determination of copper in German silver are given in § 435.

418. Examples.

1. The copper in a 2.0062 g. sample of an alloy was quantitatively deposited by electrolysis. The cathode plus the deposit weighed 6.4021 g. After removing the deposit, the cathode weighed 6.1012 g. Calculate the per cent of Cu in the sample.

2. A sample of ore weighing 2.0052 g. was analyzed electrolytically for copper. The cathode plus the deposit weighed 10.4243 g. After removing the deposit, the cathode weighed 10.0002 g. The bismuth in the deposit was determined as Bi_2O_3. The weight of Bi_2O_3 obtained was 0.0047 g. The undeposited copper was determined as CuO. The weight of CuO obtained was 0.0079 g. A separate portion of the original sample weighing 2.0010 g. was dried to constant weight at 110°. After drying, it weighed 1.9610 g. Calculate the per cent of Cu in the ore on the dry basis.

CHAPTER XXI

ANALYSIS OF NON-FERROUS AND FERROUS ALLOYS

419. General Considerations. — The use of alloys has now become so widespread that the chemist is perhaps more often called upon to analyze this class of products than any other class. Many new types of alloys have been developed in recent years and others are being developed at the present time so that the chemist is often confronted with the analysis of new combinations of metals in which the percentages of the metals present vary through a wide range. New and often complicated analytical separations must be developed to meet the requirements of a quantitative analysis of these materials.

The great difficulty in alloy analysis is to obtain satisfactory and quantitative separations, as practically all the precipitations involve more or less co-precipitation of other substances. This necessarily requires purification of the precipitates, and this purification is usually very troublesome and not·always satisfactory. A procedure designed for a particular combination of elements may fail entirely if the combination is varied by the introduction of other elements, even in small amounts. An intelligently planned quantitative analysis presupposes an approximate knowledge of all the substances present. If this knowledge is not at hand then a qualitative analysis must be performed to determine what elements are present in the sample. If this is not done the errors which may be introduced by some of the elements present may be large. A quantitative analysis of an alloy has little value when the results of a qualitative analysis are not at hand.

420. Classification of Alloys. — Alloys may be divided into two classes as follows:

> Non-ferrous
> Ferrous

Under non-ferrous alloys are included those given in Table 63.

Table 63

Some Non-ferrous Alloys

Alloys[1]	Composition							
Brasses................... Cu	Zn	Sn	Pb	(Fe)				
Bronzes................... Cu	Sn	Zn	Pb	P				
Copper-nickel alloys .... Cu	Ni							
Nickel-silver (German silver). Cu	Zn	Ni	(Fe	Sn	Pb)			
Aluminum bronzes.......... Cu	Al	Fe	Zn	Ni				
Copper-manganese alloys.... Cu	Mn	Fe	Zn	Sn	Ni			
Aluminum alloys........... Al	Cu	Zn	Mn	Mg	Ni	Fe	Si	
Tin base alloys[2]............ Sn	Sb	Cu	Pb					
Lead base alloys[3].......... Pb	Sn	Sb	Cu					
Zinc base alloys............ Zn	Cu	Sn	Sb	Pb				
Fusible metals.............. Bi	Sn	Pb	Cd					
Silver alloys................ Ag	Cu	Zn	(Sn	Ni)				
Gold alloys................ Au	Ag	Cu						
Platinum alloys............ Pt	Au	Ag	(Ir	Rh	Pd	Ni	Zn)	
Heat-resisting alloys........ Ni	Cr	Fe	Cu	Mn				
Non-corrosive alloys........ Fe	Cr	Co	Ni	Cu	Fe			
Non-corrosive alloys........ Fe	Si	Mn						

For a more complete list of alloys see "Engineering Alloys," by Woldman and Dornblatt, American Society for Metals, (1936).[4]

Under ferrous alloys are included the alloy steels, and products like ferro-manganese, ferro-phosphorus, ferro-silicon, etc., which differ from the alloy steels in that their content of the alloying metal is much greater. The alloy steels are those which contain, in addition to the usual five elements; carbon, manganese, silicon, sulfur and phosphorus, one or more of the following elements; chromium, vanadium, titanium, molybdenum, tungsten, and nickel.

[1] This classification of alloys is taken from W. Campbell, "A List of Alloys," see reference, § 1.

[2] Chiefly comprises the bearing metals, Britannia metals and pewters.

[3] Chiefly comprises the bearing metals, solders and type metals.

[4] The reader should refer to this publication for the percentage compositions of the various alloys.

The specifications adopted by the Society of Automotive Engineers [5] for alloy steels are given in Table 64. These specifications give the analyst a fair idea of what he may expect to encounter in analysis.

Table 64

SOME FERROUS ALLOYS

Chromium Steels *

S.A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.	Chromium Range
5120	0.15–0.25	0.30–0.60	0.040	0.050	0.60–0.90
5140	0.35–0.45	0.60–0.90	0.040	0.050	0.80–1.10
5150	0.45–0.55	0.60–0.90	0.040	0.050	0.80–1.10
52100	0.95–1.10	0.20–0.50	0.030	0.035	1.20–1.50

Chromium-Vanadium Steels '

S.A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.	Chromium Range	Vanadium	
						Min.	Desired
6115	0.10–0.20	0.30–0.60	0.040	0.050	0.80–1.10	0.15	0.18
6120	0.15–0.25	0.30–0.60	0.040	0.050	0.80–1.10	0.15	0.18
6125	0.20–0.30	0.60–0.90	0.040	0.050	0.80–1.10	0.15	0.18
6130	0.25–0.35	0.60–0.90	0.040	0.050	0.80–1.10	0.15	0.18
6135	0.30–0.40	0.60–0.90	0.040	0.050	0.80–1.10	0.15	0.18
6140	0.35–0.45	0.60–0.90	0.040	0.050	0.80–1.10	0.15	0.18
6145	0.40–0.50	0.60–0.90	0.040	0.050	0.80–1.10	0.15	0.18
6150	0.45–0.55	0.60–0.90	0.040	0.050	0.80–1.10	0.15	0.18
6195	0.90–1.05	0.20–0.45	0.030	0.035	0.80–1.10	0.15	0.18

* Silicon range of all S.A.E. basic open hearth alloy steels shall be 0.15–0.30. For electric and acid open hearth alloy steels, the silicon content shall be 0.15 minimum.

[5] "S.A.E. Handbook," Section 2, Part III, Chemical Compositions. Society of Automotive Engineers, Inc., New York, 1938.

Table 64 — *Continued*

Nickel Steels *

S.A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.	Nickel Range
2015	0.10–0.20	0.30–0.60	0.040	0.050	0.40–0.60
2115	0.10–0.20	0.30–0.60	0.040	0.050	1.25–1.75
2315	0.10–0.20	0.30–0.60	0.040	0.050	3.25–3.75
2320	0.15–0.25	0.30–0.60	0.040	0.050	3.25–3.75
2330	0.25–0.35	0.50–0.80	0.040	0.050	3.25–3.75
2335	0.30–0.40	0.50–0.80	0.040	0.050	3.25–3.75
2340	0.35–0.45	0.60–0.90	0.040	0.050	3.25–3.75
2345	0.40–0.50	0.60–0.90	0.040	0.050	3.25–3.75
2350	0.45–0.55	0.60–0.90	0.040	0.050	3.25–3.75
2515	0.10–0.20	0.30–0.60	0.040	0.050	4.75–5.25

Nickel-Chromium Steels '

S.A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.	Nickel Range	Chromium Range
3115	0.10–0.20	0.30–0.60	0.040	0.050	1.00–1.50	0.45–0.75
3120	0.15–0.25	0.30–0.60	0.040	0.050	1.00–1.50	0.45–0.75
3125	0.20–0.30	0.50–0.80	0.040	0.050	1.00–1.50	0.45–0.75
3130	0.25–0.35	0.50–0.80	0.040	0.050	1.00–1.50	0.45–0.75
3135	0.30–0.40	0.50–0.80	0.040	0.050	1.00–1.50	0.45–0.75
3140	0.35–0.45	0.60–0.90	0.040	0.050	1.00–1.50	0.45–0.75
X3140	0.35–0.45	0.60–0.90	0.040	0.050	1.00–1.50	0.60–0.90
3145	0.40–0.50	0.60–0.90	0.040	0.050	1.00–1.50	0.45–0.75
3150	0.45–0.55	0.60–0.90	0.040	0.050	1.00–1.50	0.45–0.75
3215	0.10–0.20	0.30–0.60	0.040	0.050	1.50–2.00	0.90–1.25
3220	0.15–0.25	0.30–0.60	0.040	0.050	1.50–2.00	0.90–1.25
3230	0.25–0.35	0.30–0.60	0.040	0.050	1.50–2.00	0.90–1.25
3240	0.35–0.45	0.30–0.60	0.040	0.050	1.50–2.00	0.90–1.25
3245	0.40–0.50	0.30–0.60	0.040	0.050	1.50–2.00	0.90–1.25
3250	0.45–0.55	0.30–0.60	0.040	0.050	1.50–2.00	0.90–1.25
3312	max. 0.17	0.30–0.60	0.040	0.050	3.25–3.75	1.25–1.75
3325	0.20–0.30	0.30–0.60	0.040	0.050	3.25–3.75	1.25–1.75
3335	0.30–0.40	0.30–0.60	0.040	0.050	3.25–3.75	1.25–1.75
3340	0.35–0.45	0.30–0.60	0.040	0.050	3.25–3.75	1.25–1.75
3415	0.10–0.20	0.30–0.60	0.040	0.050	2.75–3.25	0.60–0.95
3435	0.30–0.40	0.30–0.60	0.040	0.050	2.75–3.25	0.60–0.95
3450	0.45–0.55	0.30–0.60	0.040	0.050	2.75–3.25	0.60–0.95

Table 64 — *Continued*

Manganese Steels *

S.A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.
T1330	0.25–0.35	1.60–1.90	0.040	0.050
T1335	0.30–0.40	1 60–1.90	0.040	0.050
T1340	0.35–0.45	1.60–1.90	0.040	0.050
T1345	0.40–0.50	1.60–1.90	0.040	0.050
T1350	0.45–0.55	1.60- 1.90	0.040	0.050

Molybdenum Steels *

S A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.	Chromium Range	Nickel Range	Molybdenum, Max.
4130	0.25–0.35	0.50–0.80	0.040	0.050	0.50–0.80	....	0.15–0.25
X4130	0.25–0.35	0.40–0.60	0.040	0.050	0.80–1.10	....	0.15–0.25
4135	0.30–0.40	0.60–0.90	0.040	0.050	0.80–1.10	....	0.15–0.25
4140	0.35–0.45	0.60–0.90	0.040	0.050	0.80–1.10	....	0.15–0.25
4150	0.45–0.55	0.60–0.90	0.040	0.050	0.80–1.10	....	0.15–0.25
4340	0.35–0.45	0.50–0.80	0.040	0.050	0.50–0.80	1.50–2.00	0.30–0.40
4345	0.40–0.50	0.50–0.80	0.040	0.050	0.60–0.90	1.50–2.00	0.15–0.25
4615	0.10–0.20	0.40–0.70	0.040	0.050	....	1.65–2.00	0.20–0.30
4620	0.15–0.25	0.40–0.70	0.040	0.050	....	1.65–2.00	0.20–0.30
4640	0.35–0.45	0.50–0.80	0.040	0.050	....	1.65–2.00	0.20–0.30
4815	0.10–0.20	0.40–0.60	0.040	0.050	....	3.25–3.75	0.20–0.30
4820	0.15–0.25	0.40–0.60	0.040	0.050	....	3.25–3.75	0.20–0.30

Silicon Manganese Steels

S.A.E. No.	Carbon Range	Manganese Range	Phosphorus, Max.	Sulfur, Max.	Silicon Range
9255	0.50–0.60	0.60–0.90	0.040	0.050	1.80–2.20
9260	0.55–0.65	0.60–0.90	0.040	0.050	1.80–2.20

Table 64 — *Continued*

Tungsten Steels *

S.A.E. No.	Carbon Range	Manganese, Max.	Phosphorus, Max.	Sulfur, Max.	Chromium Range	Tungsten Range
71360	0.50–0.70	0.30	0.035	0.040	3.00–4.00	12.00–15.00
71660	0.50–0.70	0.30	0.025	0.040	3.00–4.00	15.00–18.00
7260	0.50–0.70	0.30	0.035	0.040	0.50–1.00	1.50– 2.00

Corrosion and Heat Resisting Alloys

S.A.E. No.	Carbon, Max.	Manganese, Max.	Silicon, Max.	Phosphorus, Max.	Sulfur, Max.	Chromium Range	Nickel Range
30905	0.08	0.20–0.70	0.75	0.030	0.030	17.00–20.00	8.00–10.00
30915	0.09–0.20	0.20–0.70	0.75	0.030	0.030	17.00–20.00	8.00–10.00
51210	0.12	0.60	0.50	0.030	0.030	11.50–13.00	. . . .
X51410	0.12	0.60	0.50	0.030	0.15–0.50	13.00–15.00	. . . .
51335	1.25–0.40	0.60	0.50	0.030	0.030	12.00–14.00	. . . .
51510	0.12	0.60	0.50	0.030	0.030	14.00–16.00	. . . .
51710	0.12	0.60	0.50	0.030	0.030	16.00–18.00	. . . .

It is too far beyond the scope of this book to consider in any extended manner the general subject of the analysis of non-ferrous and ferrous alloys, so that for information in this regard the reader must consult special works, such as Blair, Griffin, and Moore, cited in § 11, also the works of Ibbotson and Aitchison,[6] Price and Meade,[7] and Wölbling.[8] It will suffice for our purposes to take up three examples under the non-ferrous alloys and one under the ferrous alloys. For the former, we will select the

[6] F. Ibbotson and L. Aitchison, "Analysis of Non-ferrous Alloys," 2nd ed., Longmans, Green & Co., New York, 1922.

[7] W. B. Price and R. K. Meade, "Technical Analysis of Brass and Non-ferrous Alloys," 2nd ed., John Wiley & Sons, Inc., New York, 1917.

[8] H. Wölbling, "Die Bestimmungsmethoden des Arsens, Antimons und Zinns, und ihre Trennung von anderen Elementen," F. Enke, Stuttgart, 1914.

analysis of a brass, a solder and a German silver, and for the latter the analysis of a tungsten steel.

421. Exercise No. 49.   Analysis of a Brass (Cu, Zn, Sn, Pb, Fe). — For the majority of brasses, it is seldom that the percentages of the components will lie outside of the following values:

Cu	Zn	Sn	Pb	Fe
50–90 %	20–40 %	0–6 %	0–2 %	0–3 %

All the foregoing elements are usually determined on the same portion.   The amount of sample to be taken for analysis is governed by the content of tin and should be such as to contain about 50–60 mg. of that element.   If no information as to the content of tin is available, weigh out 3 g. of sample.

422. *Determination of Tin.* — Weigh out into a 250 ml. beaker an amount of clean alloy containing 50–60 mg. of tin.   If nothing is known concerning the tin content, weigh out 3 g. of sample. Add 40 ml. of 8 M nitric acid, cover immediately with a watch-glass and, when violent action ceases, boil until no more red fumes are given off.   Place the beaker on the steam-plate or water-bath and digest for 30 minutes, without, however, evaporating to dryness.   During the solution of the alloy, the following reaction takes place,

$$Sn + 4\,H^+ + 4\,NO_3^- \rightarrow H_2SnO_3 + 4\,NO_2 + H_2O.$$
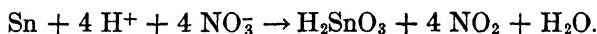
Filter off the impure metastannic acid through filter paper and wash it thoroughly with 0.2 M nitric acid, testing the last few drops of each washing after the fourth with 0.2 M potassium ferrocyanide solution or with 0.2 M ammonium sulfide solution until no precipitate or coloration is given by either of these reagents.   Transfer the filter paper and its contents to a weighed porcelain crucible and ignite it, gently at first, with the Bunsen flame and then strongly by means of the Meker burner; cool and weigh.   Repeat the ignition with the Meker burner until successive weighings check.   Calculate the weight of the impure stannic oxide.   Where a high degree of precision is not required, the impurities in the stannic oxide may be disregarded.   However, for very precise work, they may be removed and corrected for by the following method.

The stannic oxide which is obtained by the solution of the brass in nitric acid is always contaminated with small amounts of copper, lead and iron.   To separate these elements, and at the same time enable us to correct for their presence in the impure stannic oxide, we proceed as follows: Mix the impure stannic oxide in a porcelain crucible with eight times its weight of a mixture of equal parts by weight of sodium carbonate and sulfur.   Cover the crucible with its lid and heat with the low flame of the Bunsen burner until the distilled sulfur ceases to burn from under the crucible cover.   By this method, insoluble sulfides of copper, lead and iron and the soluble sodium sulfostannate, Na_2SnS_3, are formed.   Allow to cool and then place the crucible and its cover in a beaker containing sufficient water to cover both and warm in order to dissolve the melt.   After solution of the melt has been effected, remove the crucible and its lid from the solution and wash them free of adhering liquid.   Now add an excess of 0.5 M sodium sulfite solution [9] in order to decompose the polysulfides formed and digest for 10–15 minutes.   The decomposition of the polysulfides is necessary because the sulfides of copper, lead and iron which we are trying to separate are appreciably soluble in polysulfide solutions but not in normal sodium sulfide solutions.

The reaction between the polysulfides and the sulfite is:

$$Na_2S_x + (x - 1) Na_2SO_3 \rightarrow (x - 1) Na_2S_2O_3 + Na_2S.$$

Filter off on filter paper the residue, which consists of the sulfides of copper, lead and iron, wash it thoroughly with 0.1 M colorless ammonium sulfide, and ignite in a porcelain crucible.   Cool the ignited residue, which consists of CuO, PbO, and Fe_2O_3, in a desiccator; then weigh.   This weight, deducted from the weight of the impure stannic oxide, gives the weight of stannic oxide corresponding to the tin present in the sample.   If the ignited residue weighs more than several milligrams, it is likely that SnO_2 is present in it as a result of imperfect fusion of the impure stannic oxide with the mixture of sodium carbonate and sulfur.   In such an event, the ignited residue should be fused with eight times its

[9] This solution should be prepared in small quantity as needed;   it does not keep on standing.

weight of the mixture of sodium carbonate and sulfur, the melt extracted with water, as before, the sulfides of Cu, Pb, and Fe filtered off and again ignited and weighed. A blank should be run on the fusion mixture of sodium carbonate and sulfur, because the sulfur usually contains iron as an impurity.

Dissolve the ignited residue in 1–2 ml. of 6 M nitric acid and add it to the main filtrate containing the copper, lead and zinc.

An alternative method [10] of determining the weight of SnO_2 in the impure stannic oxide may be used. In this method, determine the weight of the impure stannic oxide in the porcelain crucible and add fifteen times its weight of NH_4I. Heat at $425°$–$450°$ in a muffle furnace to drive off the tin as SnI_4. When all fumes have been driven off, cool and add 2–3 ml. of 16 M HNO_3. Heat cautiously at first to convert any iodides to oxides, and continue heating to constant weight. Cool in a desiccator and weigh. The loss in weight of the crucible and contents represents the SnO_2 which was present. From the weight of SnO_2 and the weight of the original sample, calculate the per cent of Sn in the sample. Dissolve the oxides remaining in the crucible by adding a few milliliters of 12 M HNO_3. Add this solution to the main solution containing the copper, lead and zinc.

423. Determination of Copper and Lead. — There are two alternative ways of proceeding with the analysis of the main filtrate, after adding to it the copper, lead and iron recovered from the impure stannic oxide. These alternative methods we will designate as *Method A* and *Method B*. Method A requires less time than Method B. In the determination of copper by either method, it is preferable not to work upon the whole solution, but rather to make it up to definite volume and then to take an aliquot portion corresponding to about 200 mg. of copper.

424. Method A for the Determination of Copper and Lead. — According to Method A, the copper and lead from the same solution are plated out by electrolysis, the lead being plated out at the anode, after which the copper is plated out at the cathode. This method requires that the anode which is used in the determination of lead and the cathode used in the determination of copper shall be platinum gauze electrodes, each having a total

[10] Caley and Burford, *Ind. Eng. Chem., Anal. Ed.,* **8,** 114 (1936)

surface of about 150–200 cm.². The details of the method are as follows:

Having added to the main filtrate the copper, lead and iron recovered from the impure stannic oxide, transfer it to an electrolytic beaker and add enough water to bring the level of the solution just up to the top of the gauze portion of the electrodes; then add enough 16 M nitric acid to the solution to make the final concentration of this reagent 1.5 M. Arrange the electrolytic set-up as described in §§ 408–410 and in § 414 *et seq.*, but with the exception that the gauze electrode is to be attached to the positive terminal and the spiral wire is to be attached to the negative terminal. Support the beaker in such a manner that it can be lowered away from the electrodes and removed clear of them. Also make sure that sufficient stirring is provided; electrolyze the solution with an initial current density of 0.01 amp./cm.², gradually increasing it to 0.015 amp./cm.². At the end of two hours, stop the stirring, but do not at the moment turn off the current passing through the electrolyte. Lower the beaker away from the electrodes, rinsing both the latter thoroughly with a fine stream of distilled water as the beaker recedes from them. As soon as the beaker is clear of the electrodes, set it aside temporarily, turn off the current, and wash the anode with distilled water. Then treat it as follows:

Pour over the anode some 95% alcohol in order to remove any adhering water, and immediately place it in an oven or air-bath (§ 20) which has a temperature of 180°–230° and allow it to remain for 30 minutes. At the end of this time, transfer it to a desiccator, allow to cool, and weigh. This weight gives the weight of the anode plus that of the deposited lead peroxide. After being weighed, treat the anode with 6 M nitric acid and a few milliliters of hydrogen peroxide to dissolve the lead peroxide, wash with distilled water, then with 95% alcohol, dry at 180°–230° as before, allow to cool in the desiccator and weigh. The difference between the two weights gives the weight of lead peroxide. From this latter value calculate the weight of lead by means of the empirical factor 0.864. This factor is used instead of the theoretical factor 0.866 because the deposited lead peroxide, even after drying at 180°–230°, retains some water and

hence its composition is slightly divergent from the formula PbO_2 in that the ratio of lead to the rest of the compound is a trifle low.[11]

Make up the solution containing the copper to a definite volume and take for analysis an aliquot containing about 200 mg. of copper. Bring the volume of the aliquot to about 100 ml. by dilution or by evaporation and cautiously neutralize the cold solution with 8 M NH_4OH solution. Add 20 ml. of 8 M HNO_3 solution and titrate to a faint pink with 0.02 M $KMnO_4$ solution. Dilute to 200 ml. and add 10 ml. of 3% H_2O_2 solution. Transfer the spiral wire electrode to the positive terminal and electrolyze as described in § 416.

On completion of the electrolysis, and with the current still on, wash the electrodes with water from the wash bottle while lowering the beaker containing the electrolyte. As soon as the beaker is clear of the electrodes, set it aside temporarily, turn off the current and remove the cathode. Pour over it some 95% alcohol so as to remove any adhering water, then place it in an electric oven at 105°–110° and allow it to remain until the alcohol is evaporated, but no longer. This will require from 1 to 2 minutes. Transfer the electrode to a desiccator, allow it to cool and weigh. This weight gives the weight of the cathode plus deposited copper and it may also include 0.1–0.5 mg. of platinum which may have dissolved from the anode. After the weighing, treat the cathode with 6 M nitric acid to dissolve the copper, wash with distilled water, then with 95 % alcohol, dry at 105°–110° for 1–2 minutes as before, allow it to cool in a desiccator and weigh. The difference between the two weights gives the weight of deposited copper.

If the weight of the deposited copper is in the neighborhood of 200 mg., the electrolyte will probably still contain 3–5 mg. of copper,[12] but almost surely no lead. To determine this residual

[11] Cf. R. O. Smith, $J. Am. Chem. Soc.$, **27**, 1287 (1905), in regard to the composition of PbO_2 as a function of the temperature and time of drying.

[12] $Nat. Bur. Standards$, "Certificate of Analysis of Standard Sample No. 37, Sheet Brass," (Jan., 1914), reports that, in its electrolysis of the copper in said sample, it found 1–3.5 mg. of copper remaining in the electrolyte after the electrolysis; it does not apparently mention, however, the weight of the copper deposited on the cathode.

copper, bring the molarity of the nitric acid down to about 0.5 M by neutralization with 15 M ammonium hydroxide, then transfer the solution to a 750 ml. Erlenmeyer flask, warm to 50°–60° and saturate with hydrogen sulfide. Allow the solution to stand until the precipitated copper sulfide settles, then filter off the latter on a weighed porcelain Gooch crucible, wash with 0.1 M hydrochloric acid saturated with hydrogen sulfide, ignite over the Meker burner to CuO and weigh. The filtrate is saved for the determination of the iron and zinc. Calculate the weight of Cu corresponding to the CuO and add it to the weight of copper found by electrolysis.

If the weight of deposited copper is much over 200 mg. in consequence of a large sized aliquot having been taken, the electrolyte may contain 10–20 mg. of copper after electrolysis. To determine this copper, replace the electrolyte in the circuit, insert the clean electrodes, after having previously ignited them for a few minutes, and resume the electrolysis for 30 minutes, employing the same technique to terminate the electrolysis as has just been described above. Weigh any copper that plates out. Whatever copper is found here must, of course, be added to the amount previously found. Even after this second electrolysis of the electrolyte, a small residual amount of copper may still remain. This must be determined by precipitation as copper sulfide with ignition to the oxide as described previously in § 424.

425. Method B for the Determination of Copper and Lead. — In Method B the lead from the whole sample is precipitated and determined as lead sulfate prior to the plating out of the copper by electrolysis from a subsequent aliquot. The details of the method are as follows:

Having added the copper, lead and iron recovered from the impure stannic oxide to the main filtrate from the impure stannic oxide, transfer the filtrate to a 250 ml. casserole, add 7–8 ml. of 18 M sulfuric acid and evaporate to fumes of sulfur trioxide in order to make sure that all the nitric acid has been expelled. The expulsion of the nitric acid is absolutely necessary because of the marked solubility of lead sulfate in nitric acid solutions, as shown by the following figures which also include the solubility

of lead sulfate in hydrochloric acid solutions. (See Mellor, p. 316 of reference given in § 11.)

Solution	Solubility of $PbSO_4$ per 100 g. Solution
2.0 M HNO_3	140 mg.
3.0 M HNO_3	350 mg.
5.0 M HNO_3	950 mg.
3.0 M HCl	330 mg.
5.0 M HCl	590 mg.

During the evaporation, the sulfates of lead, copper and zinc separate out in the solid phase so that the solution is almost sure to bump violently, particularly in the latter stages of the evaporation, unless the solution is stirred or rotated vigorously. The early stages of the evaporation can be most conveniently effected on the water-bath, the later stages over a small flame. After the solution has fumed 1–2 minutes,[13] allow it to cool, cover the casserole with a watch-glass to catch any spattering, and then add water very cautiously through the lip of the casserole. After about 75 ml. of water has been added, heat the solution to 60°–70° for several minutes to dissolve soluble salts, then add 75 ml. more of water at room temperature and set the solution aside for 30 minutes. If the specified amount of sulfuric acid was previously added, the solution will now be 0.5 M with respect to H_2SO_4. This is a favorable concentration of H_2SO_4 for the precipitation of lead sulfate, as shown by the following figures for the solubility of lead sulfate.[14]

Solution	Solubility of $PbSO_4$ per 100 g. Solution
Water	3.8 mg.
0.005 M H_2SO_4	0.6 mg.
0.05 M H_2SO_4	0.6 mg.
0.5 M H_2SO_4	0.6 mg.
13.0 M H_2SO_4	3.0 mg.

[13] The fumes of nitric acid must not be mistaken for those of sulfur trioxide.
[14] Mellor, p. 316 of reference given in § 11.

Filter off the precipitated lead sulfate on a weighed porcelain Gooch crucible and wash 5 or 6 times with 0.5 M sulfuric acid, allowing the washings to run into the filtrate. Substitute a fresh beaker to receive further washings, and wash the precipitate 5 or 6 times with 50% (by volume) alcohol to free it of sulfuric acid. These alcoholic washings are rejected. Now dry the Gooch crucible in the electric oven at 105°–110° for 20–30 minutes to free it from alcohol. The lead sulfate precipitate must be freed from alcohol by drying before the final heating because it is easily reduced to metallic lead when heated with organic matter at relatively low ignition temperatures. After the alcohol is removed, heat in the air-bath at 300°–400° for 20–30 minutes, cool in the desiccator and weigh. From the weight of $PbSO_4$, calculate the weight of Pb.

Make up the filtrate to definite volume and take an aliquot portion which will furnish about 200 mg. of copper. Evaporate the aliquot to fumes of SO_3, dilute to 200 ml. with distilled water and electrolyze with stirring and with a current density of 0.02 amp./cm.^{2} until the copper is quantitatively deposited. With the current on, lower the beaker containing the electrolyte while washing the electrodes with distilled water. The deposit may be discolored by the presence of copper sulfide and may contain small amounts of arsenic and antimony. Dissolve the deposit in 40 ml. of 4 M HNO_3 and dilute the solution to 200 ml. with distilled water. Add 10 ml. of 3% H_2O_2 solution and electrolyze as described in § 416. After electrolyzing, any undeposited copper is recovered by precipitation with H_2S as described in § 415.

426. Determination of Iron. — Iron is determined in the aliquot taken for the copper (Method A or B) after the main portion of the copper in it has been removed by electrolysis and the small residual portion has been removed by precipitation with hydrogen sulfide. In the procedure, boil off the hydrogen sulfide and oxidize the ferrous ion to ferric by means of bromine water or nitric acid. Add 10 ml. of 3 M ammonium-chloride solution and then make the solution faintly alkaline with 3 M ammonium hydroxide. Allow the precipitate of ferric hydroxide to settle. If this precipitate of $Fe(OH)_3$ represents more than several milligrams of iron, it should be redissolved and reprecipitated, because

with such large amounts of ferric hydroxide, the amount of adsorbed zinc cannot be neglected. Filter off the precipitate on filter paper, washing with 0.01 M ammonium hydroxide. Save the filtrate and washings for the determination of zinc. Dissolve the precipitate through the filter paper by means of 0.5 M sulfuric acid, make the volume of the resulting solution up to 150 ml. with 1 M sulfuric acid, and determine iron by passing through the Jones reductor and titrating with 0.005 M $KMnO_4$ solution.

The iron may also be determined, but less accurately, by ignition of the precipitate of $Fe(OH)_3$ and weighing as Fe_2O_3.

427. *Determination of Zinc.* — Determine the zinc in the filtrate from the iron determination either by precipitating it as zinc sulfide, transposing the sulfide to sulfate and weighing the latter according to the directions in § 263 or by precipitating the zinc as zinc ammonium phosphate and weighing the latter according to the directions in § 264.

428. Exercise No. 50. Analysis of a Solder (Pb, Sn, Sb). — The kind of solders which we will consider here are those which come under the classification of lead-base alloys. Their composition as given by W. Campbell,[15] is presented in Table 65.

Table 65

LEAD-BASE ALLOYS

	Pb	Sn	Sb
Solder.........................	60 %	39 %	1 %
Plumber's.	66.6	33.3	
Half and half.	50	50	
Tinman's.....................	33.3	66.6	

Usually a small amount of antimony will always be found present as an impurity. The lead and tin are determined in one portion and the antimony in another. The details of procedure follow herewith.

429. *Determination of Tin.* — Dissolve 0.5 g. of the sample in a 200 ml. beaker with 20 ml. of 8 M nitric acid. Digest on the hot-plate for one hour or more, but do not allow the solution to

[15] See footnote 3, § 1.

evaporate to dryness. Next add 50 ml. of hot water and, after the
precipitate of impure stannic oxide has settled, filter it off on
filter paper and wash thoroughly with 0.2 M nitric acid, testing
the last few drops of each washing after the fourth with 0.2 M
potassium ferrocyanide solution or 0.2 M ammonium sulfide
solution until no precipitate or coloration is given by either of
these reagents. Save the filtrate and washings for the deter-
mination of lead. Transfer the filter paper and its contents to
a weighed porcelain crucible and ignite it, gently at first, with the
Bunsen flame and then strongly by means of the Meker burner;
cool and weigh. Repeat the ignition with the Meker burner
until successive weighings check. Calculate the weight of impure
stannic oxide. The impurities are PbO and Sb_2O_4. The cor-·
rection for the PbO is obtained by determining the amount of
lead in the ignited stannic oxide precipitate; the correction for
the Sb_2O_4 is obtained by calculation from the amount of antimony
found to be present in the whole sample. The validity of this
latter procedure is based on the assumption that all the antimony
goes with the tin in the solution of the alloy. This assumption
for the behavior of antimony in the presence of tin is true, pro-
vided the amount of tin is at least eight times that of the antimony,
a condition which is satisfied in the present instance.

PbO in the Impure SnO_2.— Mix the impure stannic oxide in a
porcelain crucible with eight times its weight of a mixture of equal
parts by weight of sodium carbonate and sulfur, and conduct
the fusion and extraction as directed in § 422, filtering off the
PbS on filter paper and discarding the filtrate. Dissolve the
PbS through the filter paper by means of a little 3 M nitric acid,
and then either determine the lead in the solution electrolytically
as PbO_2 by the method given in § 424, or determine it as $PbSO_4$
by adding 1–2 ml. of 18 M sulfuric acid, heating to fumes of
sulfur trioxide, allowing to cool, diluting with 50 ml. of water,
allowing to stand 30 minutes, filtering off the precipitated $PbSO_4$
on a weighed Gooch crucible, and weighing. This whole pro-
cedure is carried out in accordance with the details of § 425.
From the weight of $PbSO_4$ found here, the weight of PbO to be
subtracted from the impure stannic oxide is calculated, as well
as the weight of Pb to be added to that found in the main filtrate.

Sb₂O₄ in the Impure SnO₂. — As already mentioned in § 429, the weight of Sb_2O_4 to be subtracted from the impure stannic oxide is calculated from the weight of antimony found to be present in the whole sample. The weight of antimony in the sample may be determined by the method given in § 431.

430. *Determination of Lead.* — The lead is determined in the filtrate and washings from the impure stannic oxide obtained when the original sample was treated with nitric acid. The details of this determination are given in § 425. To the amount of lead so found must be added the amount recovered from the impure stannic oxide as described in § 429.

431. *Determination of Antimony.* — Weigh out 1 g. of sample and transfer it to a 500 ml. Erlenmeyer flask (Pyrex ware is the safest to use for the ensuing operation), add 15 ml. of 18 M sulfuric acid and 4–5 g. of potassium sulfate. Heat the flask strongly over a free flame, giving it a rotatory motion during the heating. Heating with 18 M sulfuric acid brings about precipitation of lead as $PbSO_4$ and oxidizes the tin to stannic ion. It also oxidizes metallic antimony to antimonous ion, provided the heating is not carried on after all the antimony is in solution. The potassium sulfate is added in order to raise the boiling point of the solution and thereby to bring about a more rapid decomposition of the alloy. When the residue is white, the decomposition is complete. Allow the solution to cool and add 40 ml. of 1 M tartaric acid and 10 ml. of 12 M hydrochloric acid. The addition of tartaric acid and hydrochloric acid serves to keep the antimony in solution by forming the complex tartrate ion and by preventing the hydrolysis of the antimony salts. Warm the solution until the soluble portion of the residue dissolves and any sulfur dioxide is expelled. Cool the solution to room temperature to avoid rapid oxidation of chloride ion by permanganate ion in the subsequent titration of antimony. Slowly titrate at once with standard 0.02 M potassium permanganate solution until a pink color is obtained which persists for 15–20 seconds. The solution is titrated at once, because, upon standing, some antimonous ion is oxidized by atmospheric oxygen. The end point is not permanent but gradually fades, due to the slow oxidation of chloride ion to chlorine by the slight excess of permanganate ion necessary

to give the end point. From the molarity of the permanganate solution and the fact that the antimony is oxidized from the trivalent to the pentavalent state, calculate the amount of Sb present in the sample. Also calculate the corresponding amount of Sb_2O_4 and apply the necessary correction for Sb_2O_4 in the impure stannic oxide obtained in § 429.

432. Exercise No. 51. Analysis of a German Silver. — For the majority of German silvers it is seldom that the percentages of the usual components will lie outside of the following values:

Cu	Zn	Ni	Fe
50–60 %	20–30 %	15–25 %	0.5 Max.

Weigh out about 0.7 g. of alloy, place it in a 400 ml. electrolytic beaker and cover with a watch-glass. Add 20 ml. of 8 M nitric acid. When the violent action ceases, boil until no more red fumes are given off. Heat on the steam bath for 30 minutes without evaporating to dryness. If tin is present, it will precipitate as metastannic acid. Dilute the solution to 85 ml.

433. *Determination of Tin.* — If tin is present, the treatment of the alloy with nitric acid, as described above, will bring about its precipitation as metastannic acid. If a precipitate forms, filter it off through filter paper and wash it thoroughly with 0.2 M nitric acid, testing the last few drops of each washing after the fourth with 0.2 M potassium ferrocyanide solution or with 0.2 M ammonium sulfide solution until no precipitate or coloration is produced by either of these reagents. Transfer the filter paper and its contents to a weighed porcelain crucible and ignite it, gently at first, with the Bunsen flame, and then strongly by means of the Meker burner to constant weight. From the weight of stannic oxide, calculate the per cent of tin in the alloy.

434. *Determination of Lead.* — After dissolving the original sample of alloy and filtering off any metastannic acid precipitate formed, if lead is to be determined, transfer the solution to a 250 ml. casserole and add 7–8 ml. of 18 M sulfuric acid and bring about the precipitation of any lead which may be present as $PbSO_4$ by the method described in § 425. From the weight of $PbSO_4$ obtained, calculate the per cent of Pb in the sample.

435. *Determination of Copper.* — If the test for lead is omitted, so that H_2SO_4 is absent, dilute to 200 ml., add 10 ml. of 3% H_2O_2 and electrolyze as directed in § 416. If the copper solution also contains H_2SO_4 cautiously neutralize with 8 M NH_4OH. Add 20 ml. of 8 M HNO_3, dilute to 200 ml., add 10 ml, of 3% H_2O_2 and electrolyze with stirring and with a current density of 0.02 amp./cm.^{2}, till copper is quantitatively deposited. With the current on, wash the electrodes with water while lowering the beaker. When the electrodes are clear of the solution, shut off the current. If the deposit is not discolored by copper sulfide, wash, dry, and weigh the cathode and deposit as directed in § 416 and complete the determination of copper as in § 416. If, however, the deposit is discolored, dissolve it in 40 ml. of 4 M HNO_3, dilute to 200 ml., add 10 ml. of 3% H_2O_2 and electrolyze as in § 416.

436. *Determination of Nickel.* — For just one metal use all of the solution from § 435. For nickel and zinc, dilute to 500 ml., transfer a 250 ml. aliquot to a 750 ml. beaker for nickel, add citric acid and complete as in § 279. Save the other aliquot for zinc.

437. *Determination of Zinc.* — Determine zinc by precipitating as ZnS as in § 259, and either transposing it to $ZnSO_4$ and weighing as in § 263, or by dissolving it in HCl and precipitating as $ZnNH_4PO_4 \cdot H_2O$ and weighing as $ZnNH_4PO_4$ according to § 264.

438. *Determination of Iron.* — Weigh a separate 2 g. sample, dissolve in 20 ml. of 8 M HNO_3, heat to remove all red fumes and dilute to 200 ml. Filter off and wash any metastannic acid as in § 433. To the filtrate and washings add 8 M NH_4OH to slight excess. Filter, dissolve the precipitate in 3 M HNO_3, dilute to 100 ml. and add 8 M NH_4OH to slight excess. Remove the precipitate on quantitative filter paper. Ignite in a weighed crucible to Fe_2O_3 and weigh.

439. Exercise No. 52. Analysis of a Tungsten Steel. — In addition to iron and tungsten these steels usually contain chromium, manganese, silicon, sulfur, phosphorus and carbon. (See § 420). These components and tungsten will now be considered.

440. *Determination of Silicon.* — In a 600 ml. beaker, dissolve 2 g. of sample in 50 ml. of 12 M hydrochloric acid, and when dissolved add 5–10 ml. of 16 M nitric acid, a little at a time, and digest until the residue (WO_3) is a bright, canary yellow. Evaporate to

dryness but do not bake. Redissolve in 20 ml. of 12 M hydrochloric acid, add a few drops of 16 M nitric acid and boil for a few minutes until the iron appears to be all in solution, then add 100 ml. of hot water and heat for a few minutes. Filter through filter paper and wash thoroughly with 2 M hydrochloric acid; save the filter paper and its contents. Evaporate the filtrate to dryness and bake at 105°–110° to render the silica insoluble. Take up in 15 ml. of 12 M hydrochloric acid, dilute with 100 ml. of boiling water and filter through a fresh filter paper, washing with 2 M hydrochloric acid as before; save this filtrate for the determination of phosphorus. Dissolve in a few milliliters of 3 M ammonium hydroxide any tungstic acid which adheres to the beaker in the first filtration and evaporate to dryness in a platinum crucible. Into this crucible introduce the two filter papers containing the tungstic acid and silica, ignite the whole at a dull-red heat [16] and weigh. Introduce 3–4 drops of 9 M sulfuric acid and 10–15 ml. of hydrofluoric acid and evaporate in an air-bath (§ 20) until the sulfuric acid has been driven off, and then ignite at a dull-red heat and weigh again. The loss in weight gives the weight of SiO_2, from which the weight of silicon is calculated.

441. *Determination of Tungsten.* — Fuse the residue of $WO_3 +$ Fe_2O_3 in the crucible with six times its weight of sodium carbonate, and leach the melt with hot water. Filter off the insoluble ferric oxide on a filter paper and wash well with hot water. The fusion converts the tungstic oxide into the soluble sodium tungstate, but does not affect the ferric oxide. Wash the crucible well with hot water. Since the residue on the filter paper may still contain a little tungstic oxide, return the paper and the residue to the crucible, ignite and fuse again with a small amount of sodium carbonate. Leach the melt as before, collect the residue of Fe_2O_3 on a filter paper, wash it well, then ignite it and weigh it in the same crucible. This crucible in the meantime should have been thoroughly rewashed. The difference between this weight and the weight after volatilization of the silica gives the weight of WO_3, from which the weight of tungsten is calculated.

[16] The tungstic oxide which results from the dehydration of the tungstic acid is slowly volatilized at a bright red heat.

442. *Determination of Chromium.* — The method of determining chromium is substantially that recommended by the American Society for Testing Materials.[17]

Use for the analysis 2 g. of sample when the steel contains 2% or less of chromium, and use 1 g. of sample when the chromium content is $2\text{-}5\%$. Dissolve the sample in about 60 ml. of a mixture of 19 ml. of 9 M H_2SO_4 and 5 ml. of 15 M H_3PO_4 in 36 ml. of water. Heat until the action ceases, cautiously add 10 ml. of 8 M HNO_3 and boil to expel all oxides of nitrogen and, if possible, to dissolve all carbides. Evaporate until salts begin to separate and dilute with 50 ml. of warm water. Add 5-10 ml. of 8 M HNO_3 and carefully evaporate again until salts begin to separate. If carbides still remain undissolved, filter through filter paper, wash with warm water, ignite and then fuse with sodium carbonate. Add the solution of the melt to the main solution, dilute to 300 ml. with hot water and then add 5 ml. of 0.6 M $AgNO_3$ solution and 20 ml. of 0.66 M ammonium persulfate solution. Boil for 8-10 minutes. If the pink color of permanganate ion, formed from the manganese in the sample, does not develop, add more $AgNO_3$ and $(NH_4)_2S_2O_8$ and boil for 10 minutes. Add 5 ml. of 4 M HCl to destroy the permanganate and boil for 5 minutes after the pink color of permanganate has disappeared. If the color remains after 10 minutes of boiling or if MnO_2 remains as a precipitate, add 2-3 ml. more of 4 M HCl and boil as before. The total time of boiling after adding the $(NH_4)_2S_2O_8$ should be 15-30 minutes. Cool the solution, dilute it to 400 ml. and add from a burette a measured excess of a solution of ferrous sulfate prepared by dissolving 32 g. of $FeSO_4$·$(NH_4)_2SO_4$·$6H_2O$ in a mixture of 50 ml. of H_2SO_4 and 950 ml. of water. Add about 25 ml. of this solution when the steel contains 1.5% or less of chromium, and a proportionately larger volume of solution for steels containing more than 1.5% of chromium. Stir the solution and titrate with standard $KMnO_4$ solution which is approximately 0.13 M. The end point is reached when the pink color of permanganate remains for one minute when the solution is stirred continuously.

[17] "A. S. T. M. Methods of Chemical Analysis of Metals," p. 36, American Society for Testing Materials, Philadelphia, 1936.

A blank must be run and a correction applied to the titration. The method of obtaining the blank is as follows: Boil the solution after the titration for 10 minutes to destroy the small excess of permanganate and titrate with $KMnO_4$ solution.

The procedure for standardizing the ferrous sulfate solution is as follows: Measure carefully from a burette about 25 ml. of the ferrous sulfate solution, dilute to 350 ml. with a cool solution of 0.9 M H_2SO_4 and add 2 ml. of 15 M H_3PO_4 solution. Titrate with the $KMnO_4$ solution. To obtain the blank for the standardization titration, titrate with $KMnO_4$ solution the same amount of water and acid used in the standardization. Deduct the blank from the volume of $KMnO_4$ solution used in the standardization. The standardization of the ferrous sulfate solution should be performed on the same day as the determination of chromium.

443. Determination of Manganese. — In determining manganese, the manganous ion is oxidized to permanganate ion by an excess of bismuthate ion in accordance with the following:

$$2\,Mn^{++} + 5\,BiO_3^- + 14\,H^+ \rightarrow 2\,MnO_4^- + 5\,Bi^{+++} + 7\,H_2O.$$
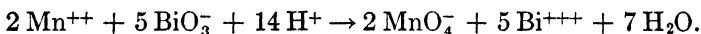
The permanganate ion is then reduced to manganous ion by adding an excess of a standard solution of ferrous ion, thus:

$$MnO_4^- + 5\,Fe^{++} + 8\,H^+ \rightarrow Mn^{++} + 5\,Fe^{+++} + 4\,H_2O.$$
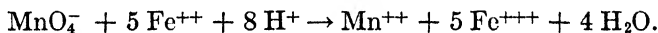
The excess of ferrous ion is then determined by titration with standard permanganate solution. From these results the weight of manganese present is obtained. The details of this method follow. Dissolve 1 g. of sample in 10 ml. of 6 M H_2SO_4 and 25 ml. of water. Add 1 M $NaHCO_3$ to the hot solution until a slight permanent precipitate is obtained, then 4 ml. more. Boil for one minute, filter through a fluted filter and wash. Add to the filtrate 12.5 ml. of 16 M nitric acid and evaporate to a volume of 50 ml. Allow it to cool to room temperature, treat with an excess of sodium bismuthate, agitate and let stand for a few minutes. Add 50 ml. of 0.5 M nitric acid and filter through a Gooch crucible. Wash the sodium bismuthate on the filter with 0.5 M nitric acid until the washings run through, colorless. Add 3 ml. of 15 M phosphoric acid to the filtered solution, and titrate the permanganate ion by adding a measured amount of standard 0.03 M

ferrous ammonium sulfate solution known to be in excess. Then titrate the excess ferrous ion by means of standard 0.006 M potassium permanangate solution. Calculate the weight of manganese accordingly.

444. *Determination of Sulfur.* — In a 400-ml. beaker, dissolve 5 g. of the sample in a mixture of 40 ml. of 16 M nitric acid and 5 ml. of 12 M hydrochloric acid; as soon as solution has been effected, add 0.5 g. of sodium carbonate (free from sulfate) and evaporate the solution to dryness, but do not bake. Add 40 ml. of 12 M hydrochloric acid, boil for a few minutes until all the iron appears to be in solution, then add 100 ml. of hot water and heat for a few minutes. Filter through filter paper and wash several times with 2 M hydrochloric acid. Evaporate the filtrate to dryness and bake at 105°–110° to render the silica insoluble. Take up in 30 ml. of 12 M hydrochloric acid and evaporate to a syrup, add 3 ml. of 12 M hydrochloric acid and 40 ml. of hot water, filter through filter paper and wash with hot water, keeping the washings below 100 ml. Allow the solution to cool to room temperature, add 10 ml. of 0.25 M barium chloride solution and let stand 24 hours. Filter off the barium sulfate through a weighed Gooch crucible (which may be of porcelain), wash several times with cold water, then several times with 0.5 M hydrochloric acid until washings are free of iron, and then with hot water. Ignite over the Bunsen burner at a temperature corresponding to a dull red color, weigh as $BaSO_4$, and calculate the amount of sulfur accordingly.

445. *Determination of Phosphorus.* — The determination of phosphorus may be made on the filtrate from the tungstic acid and silica in the silicon determination (§ 440). Evaporate the filtrate two or three times nearly to dryness with 60 ml. of 16 M nitric acid, finally to a syrupy consistency, and then dissolve in 4 M nitric acid, and precipitate with molybdate solution as directed for plain carbon steels in § 228.

An alternate method for the determination of phosphorus is as follows: Dissolve the precipitate of ammonium phosphomolybdate in 2.5 M NH_4OH solution and cautiously acidify with sulfuric acid; continue the addition of the acid until the concentration of sulfuric acid in the solution is about 1 M. Now pass

the solution through a Jones reductor and titrate immediately with standard potassium permanganate solution.

In the oxidimetric method just described the molybdate ion, MoO_4^-, formed when the precipitate, $(NH_4)_3PO_4 \cdot 12\,MoO_3 \cdot 2\,HNO_3 \cdot H_2O$, was dissolved, undergoes the following change when the solution is passed through the Jones reductor,

$$3\,e + 8\,H^+ + MoO_4^- \rightarrow Mo^{+++} + 4\,H_2O$$
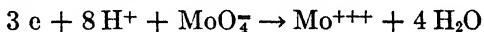
Upon titrating with potassium permanganate we have,

$$5\,Mo^{+++} + 3\,MnO_4^- + 8\,H_2O \rightarrow 5\,MoO_4^- + 3\,Mn^{++} + 16\,H^+.$$

Since
$$1\,P \equiv 12\,MoO_4^-, \text{ and } 3\,MnO_4^- \equiv 5\,MoO_4^-,$$
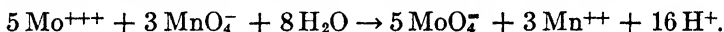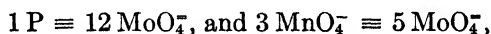
it follows that
$$36\,MnO_4^- \equiv 60\,MoO_4^- \equiv 5\,P$$
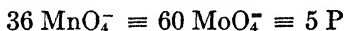
446. Determination of Carbon. — The carbon must be determined by direct combustion in oxygen at 1,100° as directed in § 449 of the next chapter.

447. Examples.

1. A 1.0012 g. sample of a non-ferrous alloy was analyzed for its constituents of Ni, W and Cr with the following results:

$WO_3 + Cr_2O_3$ impurity 0.2455 g.; Cr_2O_3 in WO_3, 0.0015 g.; Cr_2O_3 from 15/50th aliquot, 0.0982 g.; nickel dimethylglyoxime from 1/10th aliquot, 0.2885 g.

What were the percentages of the constituents?

	Ans.	Ni	58.53%
		W	19.33
		Cr	22.30
			100.16%

2. A 1.0164 g. sample of a non-ferrous alloy was analyzed for the constituents Ni, Mo and W with the following results:

WO_3, 0.3174 g. MoO_3, 0.3928 g.; nickel dimethylglyoxime from 1/10th aliquot, 0.2380 g.

	Ans.	Ni	47.56%
		Mo	27.48
		W	24.76
			99.80%

3. In the analysis of brass turnings, 5.004 g. was dissolved in 8 M HNO_3, the filtrate filtered off and the impure stannic oxide separated from its accompanying iron. The following results were obtained; Cu electrolytically, 4.043 g.; $PbSO_4$, 0.0566 g.; SnO_2, 0.3634 g.; Fe_2O_3, 0.0045 g.; $ZnSO_4$ from 1/5th aliquot, 0.3090 g. What were the percentages of the constituents?

	Ans.		
	Cu	80.80%
	Pb	.77
	Sn	5.77
	Fe	.09
	Zn	12.51
		99.94%

4. When a 0.02996 M solution of ferrous ammonium sulfate is used in the sodium bismuthate method of determining manganese in steel what per cent of manganese will be represented by 1.00 ml. of solution when a sample of 1.0000 g. is taken for analysis?

5. In determining phosphorus in a 2.017 g. sample of steel by the oxidimetric method 13.04 ml. of 0.02116 M $KMnO_4$ solution was required in the titration of the reduced molybdate. Calculate the per cent of phosphorus in the steel.

6. In determining phosphorus in steel by the oxidimetric method what per cent of phosphorus would be represented by 1.00 ml. of 0.01142 M potassium permanganate solution when a sample of steel weighing 2.0000 g. is used?

CHAPTER XXII

METHODS INVOLVING EVOLUTION AND MEASUREMENT OF GASES

448. General Considerations. — There are several very important determinations which are based upon the evolution and measurement of gases, among which are the determination of carbon dioxide in limestone and in baking powder, of carbon in steel, of nitrogen in nitrates and nitrites, of available oxygen in hydrogen peroxide, etc. In such methods, the gas is either collected by absorption in some suitable medium and the amount which is so collected is found from the gain in weight of the absorbing medium, or the gas is collected in a graduated burette and its weight is calculated from its volume, after the necessary corrections have been made for the temperature of the gas, for the barometric pressure under which it is enclosed, and for the vapor pressure of the confining liquid. For our purposes, we shall consider only the case where the gas is collected in an absorbing medium and its weight determined from the gain in weight of the absorbing medium. As examples coming under this case, we shall take up the determination of carbon in steel and of carbon dioxide in limestone.

449. Determination of Total Carbon in Steel by Direct Combustion. — In steel, carbon exists in combination with the iron in the form of various carbides, of which cementite is one of the most important. In cast iron, the carbon, in addition to being in combination with the iron, also exists as graphitic carbon. When steel or cast iron is dissolved in acid, more or less of the combined carbon is liberated as a volatile hydrocarbon and is thereby lost. To determine the total carbon, which is a matter of great technical importance, the sample of steel may either be burned directly in a rapid stream of oxygen and the resulting carbon dioxide collected; or, less preferably, the sample may be dissolved in a solution which contains, per liter, 1.7 moles

[532]

of potassium chloride, 1.7 moles of cupric chloride, and 0.1 mole of hydrochloric acid, as this solution dissolves the iron and leaves the carbon, which is then filtered off, washed, ignited to carbon dioxide, and the carbon dioxide collected and weighed. The direct combustion method is applicable to all steels, both plain carbon steels and special alloy steels, while the solution method is applicable only to plain carbon steels. Because of its general applicability, we shall describe the first method in detail, while for the details of the second method, we refer the reader to the following works: Blair, p. 156 of reference given in § 11; Griffin, *ibid.*, p. 160; Johnson, "Chemical Analysis," 3rd ed., p. 246, John Wiley and Sons, 1920.

The percentages of carbon that may be expected in various kinds of iron and steel products are as follows:

Low carbon steels	Less than 0.40 %
Medium carbon steels	0.30 % to 0.70 %
High carbon steels	0.60 % to 1.30 %
Puddled muck bar	Up to 0.15 %
Pig iron	Up to 4 %
Washed metal	Up to 4 %
Special alloy steels	Up to 1 %

The direct combustion of plain carbon steels requires a temperature of at least 1,000°. For alloy steels such as those containing chromium, molybdenum, tungsten, vanadium, etc., the temperature must be higher.[1] The greater the percentage of these elements, the more difficult it is to burn the carbon completely. In such cases where a sufficiently high temperature cannot be obtained for these special alloy steels, the sample is mixed with a fluxing material like red lead. In the presence of this substance, the combustion can be made complete at a temperature of 1,100°. If red lead is used, however, a blank must be run on it when mixed with a steel of known carbon content, because red lead is rarely free from carbon. For example, a carbon determination on a "C.P." sample of red lead gave for a 4 g. sample as much as 0.0042 g. of carbon dioxide.

[1] J. R. Cain and H. E. Cleaves, *J. Wash. Acad. Sci.*, **4**, 393 (1914), state that for chromium, tungsten, and titanium steels a temperature of 1,500° and a time of thirty minutes is necessary to oxidize the carbon by direct combustion.

The state of subdivision of the sample itself is important. The drillings should be fine and only those which pass a 20 mesh screen should be used. Any thick pieces should be discarded because there is danger of incomplete combustion during the short time ordinarily required for the complete decarbonization of the sample. The sample must, of course, be free of lint and oil.

The actual determination requires about twenty-five to thirty minutes. A two-gram sample will be decarbonized completely in three minutes at a temperature of 1,000°. In twelve to fifteen minutes more, the tube in which the combustion has taken place can be freed completely of carbon dioxide. The balance of the time is taken up in weighing.

450. Apparatus and Assembly for the Determination of Total Carbon in Steel. — The apparatus and its assembly are shown in Figure 86.

A is a steel tank which contains oxygen under pressure, and which is provided with a reducing valve, a high-pressure gauge, a low-pressure gauge, and a needle valve.

B is an electric resistance furnace which is used as a pre-heater to remove any hydrocarbons that may be present in the oxygen by oxidizing them to carbon dioxide and water. It should be capable of giving a temperature of 500°–600° and should be provided with a suitable rheostat R. The tube inserted in the pre-heater should be of pyrex glass about 36 cm. long with an inside diameter of 1.5 cm. The edges, if rough, should be fire-polished in the blast flame. The copper oxide spiral which is to go into this tube should be about 12 cm. long, and may be easily made by tightly winding 40 mesh copper gauze about a stout copper wire and folding one end of the wire up about the edge of the gauze and the other into a small loop close to the gauze. This roll is inserted in the middle of the pyrex tube and is oxidized when the pre-heater is heated. In case it is certain that oxygen which is being used for combustion purposes is free of hydrocarbons, the pre-heater may be omitted from the combustion train.

C is a U-tube with limbs about 12 cm. long by 2 cm. outside diameter. It is filled about three-quarters full with a mixture of sodium hydroxide and calcium hydroxide, known as soda lime,

LEGEND

SODA LIME = 1	COTTON
CALCIUM CHLORIDE = 2	GLASS WOOL
ZINC = 3	COPPER OXIDE GAUZE
	ASBESTOS IMPREGNATED WITH FeSO₄ IGNITED TO Fe₂O₃
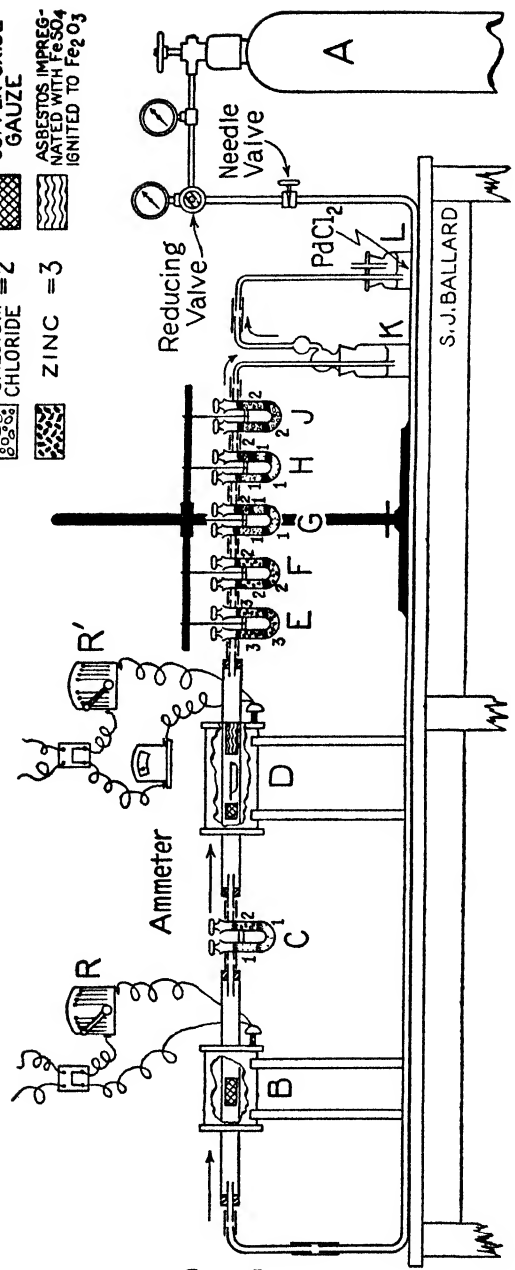
Fig. 86

Assembly for the Determination of Total Carbon in Steel

[535]

which contains 15% water. The other quarter of the tube is filled with calcium chloride. The purpose of the soda lime is to absorb carbon dioxide resulting from the oxidation of hydrocarbons in the pre-heater and the purpose of the calcium chloride is to remove any water which may be present. Tube C is filled in the following manner: The bend of the tube is filled with soda lime (12 mesh) containing 15% moisture. A wad of cotton, 0.5 cm. thick, is now placed in each limb over the soda lime. Then, in the entry limb of the tube, soda lime is placed upon the cotton until the soda lime is within 1 cm. of the bottom of the glass stopper, whereupon the remaining space is filled with cotton. In the exit end of the tube, soda lime is placed upon the cotton to a depth of about 2.5 cm., then a wad of cotton is placed on the soda lime, and above the cotton is placed the anhydrous calcium chloride (8 mesh) to within 1 cm. of the bottom of the glass stopper, whereupon the remaining space is filled with cotton. The hollow exit stopper is also filled with cotton. The ground surfaces are coated with a thin film of stop-cock lubricant and any excess is removed. Care must be taken that the exposed tops of the stoppers are wiped free of lubricant, otherwise the lubricant may be wiped away prior to weighing at the end of the determination. The calcium chloride is placed in the upper part of the limbs of the tubes, because the soda lime contains moisture to the extent of 15%. Anhydrous soda lime cannot be used because it absorbs carbon dioxide slowly and incompletely.[2] If the pre-heater is omitted from the train, C is still retained.

D is an electric furnace [3] capable of giving a sustained temperature in the neighborhood of 1,100° within the silica tube, in which the steel is burned. It should be about 25 to 30 cm. long and should have an opening about 4 cm. in diameter in order to accommodate without difficulty a silica tube having an outside diameter of 3 cm. A rheostat R' should be in series with the furnace in

[2] See Lamb, Wilson and Chaney, "Gas Masks Absorbents," *J. Ind. Eng. Chem.*, **11**, 437 (1919).

[3] The student is referred to the catalogue issued by the Hoskins Manufacturing Co., Detroit, Mich., for a detailed description of their electric combustion furnaces which are suitable for this purpose; also to the catalogue of the Burrell Technical Supply Co., Pittsburgh, which gives details of very satisfactory types of alternating current furnaces and combustion tubes.

order to regulate the current and thereby the temperature. The combustion tube should be of fused silica, glazed on the inside, about 60 cm. long and 2.5 cm. inside diameter. It is prepared for use as follows: After it has been thoroughly cleaned inside, one end is closed with a one-hole rubber stopper, a plug of glass wool is inserted, and the tube is lightly packed for a distance of 15 to 20 cm. with asbestos which has been impregnated with iron oxide and ignited for several hours at 1,000° or more. To accomplish the impregnation, 500 g. of raw asbestos are thoroughly digested in a solution which is 0.3 M with respect to ferrous sulfate and 0.1 M with respect to sulfuric acid. Upon this packing of asbestos, there is next inserted a neatly fitting plug (recently ignited) of nichrome wire or gauze to hold the asbestos in place. In the portion of the tube where the boat is to be put it is necessary to place a platinum or sheet-nickel sleeve in order to protect the tube from the incandescent particles of iron oxide which are projected during the combustion of the sample. This sleeve should fit the tube snugly and should be slightly longer than the boat; if it is made of nickel, before being inserted, it should be previously heated for two hours in a stream of oxygen at 1,000° in order to decarbonize it. The silica tube must be protected from the iron oxide because, otherwise, the iron oxide will flux with the silica and thereby ruin the tube. The boats used for the combustion should be of alundum or nickel, about 8 cm. long, 1.3 cm. deep, 1.3 cm. wide at the bottom, and 1.6 cm. wide on top. If nickel boats are used, they must previously be ignited at 1,000° for an hour or so before use. Directly preceding the boat in the inlet portion of the tube, it is necessary to place a copper spiral about 6 cm. long and similar to that described in connection with the pre-heater B.

E, F, G, H, and J are U-tubes similar in design to C. E is filled with granulated zinc (20 mesh) and covered with loose wads of glass wool. The purpose of the zinc is to remove any acidic compounds (SO_3, P_2O_5, etc.) resulting from the combustion of nonmetals, such as sulfur and phosphorus in the steel.

F is filled with calcium chloride which has been treated with dry carbon dioxide. Since many samples of anhydrous calcium chloride are alkaline, due to the presence of some calcium oxide,

the calcium chloride must first be treated with a dry stream of carbon dioxide and the excess displaced by using dry air. A sufficient amount of the treated calcium chloride is introduced into the tube by means of a short wide-stem funnel to fill the bend. This layer is now covered on each side by a loose wad of cotton about 0.5 cm. thick and some more calcium chloride is added to within 1 cm. of the bottom of the glass stopper. This intervening space is filled with a loose wad of cotton. The hollow exit stopper is charged with cotton to retain any small particles which might be carried out of the tube into its neighbor by the moving gas. The cotton wads are used in the calcium chloride in order to prevent any channeling by the gas. The ground surfaces are now given a thin coating of stop-cock lubricant sufficient to seal the joints and any excess removed with a cloth. This tube serves to remove any moisture, whether introduced into the tube with the boat or resulting from the combustion of hydrogen in the oxygen if the pre-heater is omitted.

G and H [4] are soda lime tubes, prepared in the same manner as C. They must be carefully prepared, since they are to absorb the carbon dioxide resulting from the combustion of the carbon in the steel. These tubes are weighed separately in each determination, as well as in each blank, tube H serving as a guard tube which indicates by an increase in its weight when tube G has absorbed its maximum amount of carbon dioxide.

J is filled with calcium chloride in the same manner as F. The tube J is employed between H and K, because if H and K were

_____

[4] The U-tubes, G and H, are recommended for student use in place of specially designed absorption bottles of much larger capacity. The main advantage of such bottles over the U-tubes is in the number of combustions which can be run without refilling. Since the student is rarely called upon to run more than four or five combustions, it would seem that the bottles offer no advantage over the U-tubes. We have found that two U-tubes, filled as described, will absorb as much as 3 to 4 g. of carbon dioxide. There are certain disadvantages in using the bottles; namely, that when filled, their weights are excessive, some weighing as much as 80 to 90 g. The weight has been reduced somewhat by using thin glassware, but this, in itself, makes them more fragile and, consequently, subject to shattering by the least shock, a happening which proves much more expensive to the student than does the fracturing of a U-tube.

directly connected to each other, water in the form of vapor would be abstracted from the calcium chloride in H by the sulfuric acid in K, because 18 M sulfuric acid has a much lower aqueous vapor tension than the calcium chloride. It is always safer to protect the absorption train by the same drying agent which is used in the train.

K is a bubble counter which contains 18 M sulfuric acid to the depth of about 3 cm.; the inlet tube of K, which should have an inside diameter of 0.7 cm., should be immersed to the depth of 1.6 cm. The rate of flow can be judged from the information given in Table 66.

Table 66

DATA FOR ESTIMATION OF RATE OF GAS FLOW

Inside Diameter of Inlet Tube of Bubble Counter	Size of Bubble when Liberated under a Depth of 1.6 cm. of 18 M H_2SO_4	Bubbles per Second	ml. Gas per Minute
0.5 cm.	0.17 ml.[5]	2	20
0.7 "	0.33 "	2	40

L is a small bottle containing 0.003 M palladous chloride solution; the bottle should be provided with a rubber stopper and an outlet tube. The purpose of the palladous chloride solution is to show whether any of the carbon has been incompletely burnt to carbon monoxide, this gas reacting with palladous ion so as to reduce it to finely divided black metallic palladium.

All connections in the train, except those requiring a rubber stopper, should be made by means of thick-walled pressure tubing. Tubing 1.2 cm. outside diameter with 0.3 cm. bore serves well.

An alternative arrangement is one in which C of Figure 86 is two thirds full of asbestos impregnated with sodium hydroxide, known as ascarite. The other third of C, at the exit end, contains magnesium perchlorate trihydrate, known as dehydrite. The ascarite and dehydrite in C are separated by a layer of asbestos fibre 1 cm. thick. Tubes F and J contain dehydrite and tubes G and H are replaced by an absorption bulb two thirds full of

[5] Measured at 760 mm. Hg pressure and a temperature of 25°.

ascarite with the remaining third, at the exit end, containing dehydrite. The ascarite and dehydrite in the absorption bulb are separated by a layer of asbestos fibre 1 cm. thick. The change in appearance of the ascarite as a result of its absorption of CO_2 gives an indication of the capacity of the bulb for further absorption and makes it unnecessary to use a second absorption bulb to serve as a guard.

451. Exercise No. 53. Determination of Total Carbon in Carbon Steel. — After the apparatus has been assembled as portrayed in Figure 86 and described in § 450, the procedure resolves itself into three steps, namely: running a blank, running a standard sample, and then running the unknown sample. In all these operations it is necessary to be sure of the temperature. This can be determined each time by means of a pyrometer; or a curve can be plotted giving the steady temperature of the furnace corresponding to a given amperage through it, and the temperatures determined by means of this curve.

The Blank. — Disconnect the absorption train at E, and after the furnace has reached the temperature of 1,000°–1,050°, pass through the combustion tube a stream of oxygen at the rate of 40 ml. per minute (see § 450) for about fifteen minutes. In the meanwhile, half fill the boat with RR alundum [6] which has been previously ignited at 1,000°, and then weigh out two or three grams of the fine drillings of the standard sample. Transfer these drillings to the boat and put the boat away in the desiccator. At the end of the fifteen minutes, shut off the oxygen and connect the entire train as shown in Figure 86. Set all the stop-cocks in the "running position" and pass oxygen through the entire system at the rate of 40 ml. per minute for five minutes. Then disconnect the tubes G and H (or the absorption bulb, if ascarite is used) and close their stop-cocks. Wipe them carefully (§ 87), allow to stand for ten minutes, and then weigh them separately. Reinsert the tubes in the system in the same relative position as before, with their stop-cocks open, and pass oxygen at the same rate as previously for twenty minutes. At the end of this time, disconnect the tubes, close their stop-cocks, weigh separately

[6] This material can be obtained from any of the chemical supply houses, or from the Norton Company, Worcester, Mass.

after wiping, and allow to stand for ten minutes in the same manner as before.   If the individual weights check the previous weights within 0.2 to 0.3 mg., the apparatus is ready for the combustion of the standard steel; if the weights do not come within the tolerance named, the same procedure is repeated until successive weighings do check.

The Standard Sample. — After obtaining a satisfactory blank, the working condition of the apparatus is further checked by burning a steel of known carbon content and of the same general type as the unknown sample to be run later.   If the weight of carbon found for the standard checks the weight known to be present, the apparatus is ready for the combustion of the unknown sample.   The technique in running the standard sample is exactly the same as that which is to be followed in running the unknown sample; it is as follows: After the blank has been obtained and the furnace is at the right temperature, complete the absorption train and introduce into the silica tube the boat containing the standard steel, pushing it, by means of a clean glass rod, into the sleeve in the center of the silica tube.   Place behind it the short copper spiral which was removed in order to introduce the boat, and connect the purifying tube C.   Now pass oxygen through the system at the rate of 40 ml. per minute.   The steel will begin to burn within two minutes.   During the burning, the amount of oxygen leaving the apparatus will fall off and may even cease.   As soon as there is any evidence of this, open the needle valve of the oxygen tank so as to increase the supply of oxygen during the burning period.   The combustion takes place within a few minutes and its end can be practically assumed when the rate of oxygen going through the bubble counter begins to correspond to the increased opening of the needle valve.   Close the needle valve until the rate of oxygen going through the bubble counter is reduced to 40 ml. per minute.   This rate of flow is then maintained for fifteen minutes in order to sweep out the combustion tube thoroughly.   After this sweeping-out period, shut off the oxygen, disconnect the absorption tubes G and H, or the ascarite absorption bulb if one has been used, and allow to cool.   The soda lime tubes become hot during the absorption of the carbon dioxide because the reaction between soda lime

and carbon dioxide gives off a large amount of heat. The tubes, before being weighed, must always be allowed to come to room temperature. Wipe, let stand ten minutes, and weigh. The increase in weight is due to carbon dioxide. From this increase, calculate the per cent of carbon in the standard.

The Unknown Sample. — Granting that a satisfactory result has been obtained for the standard steel, weigh out two or three grams of the fine drillings of the unknown sample and transfer it to a boat that has been previously ignited at 1,000°. Introduce the boat into the furnace and conduct the combustion in accordance with the details of the preceding paragraph. From the weight of carbon dioxide obtained, calculate the percentage of carbon in the unknown sample.

452. Determination of Carbon Dioxide in a Limestone. — The composition of limestones has already been given in § 244. The method of determining the carbon dioxide consists in adding acid to the limestone in a closed system and sweeping out the evolved carbon dioxide by means of air (free from carbon dioxide) into absorption tubes that are filled with soda lime. The gain in weight of the absorption tubes gives the weight of CO_2 in the sample.

When the acid is added to the sample, the hydrogen ion removes carbonate ion to form first the slightly dissociated bicarbonate ion and finally molecular carbonic acid, which is itself slightly ionized. This is illustrated as follows:

$$\left.\begin{array}{c} CO_3^- + H^+ \rightleftarrows HCO_3^- \\ H^+ \end{array}\right\} \rightleftarrows H_2CO_3 \overset{diss'd}{\rightleftarrows} H_2O + CO_2 \rightleftarrows CO_2 \text{ gas.}$$
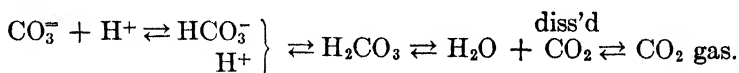
The forward action is further assisted by the fact that carbonic acid is unstable and breaks down into water and carbon dioxide. The carbon dioxide, as soon as it exceeds its solubility in water, escapes as gaseous carbon dioxide. At the beginning of the determination, before the addition of acid, we may consider the solution saturated with respect to calcium carbonate. Then we have
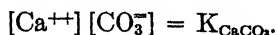
$$[Ca^{++}]\,[CO_3^-] = K_{CaCO_3}.$$

On the addition of hydrogen ion, the carbonate ion is removed as indicated above and the ion product tends to fall below K_{CaCO_3}.

With the solid phase present, however, more calcium carbonate goes into solution as illustrated by the equation

$$CaCO_3 \rightarrow Ca^{++} + CO_3^{-}.$$

As the hydrogen ion constantly removes carbonate ion, the solid calcium carbonate must gradually pass into solution until it has completely dissolved. The carbonate ion concentration at the end of the reaction is extremely minute, due to the presence of a high concentration of hydrogen ion. This minute concentration is reduced to zero upon boiling the solution to remove the carbon dioxide dissolved in the water.

453. *Apparatus and Assembly for the Determination of Carbon Dioxide in Limestone.* — Figure 87 shows an assembly which may be used in the determination of carbon dioxide in limestone. The guard tube A, 10 cm. long and 1.8 cm. in diameter, is filled with soda lime to remove carbon dioxide from the air drawn through the apparatus. It is filled as follows: The tube is held with its wide mouth on top and upon the bottom of the bulb is placed a small loose wad of cotton in order to keep any soda lime from falling through the narrow outlet tube. Sufficient soda lime (12 mesh) containing about 15% moisture is then placed on top of the cotton to within about 2 cm. of the top. The remaining space is filled with cotton which is held in place by using a two-hole rubber stopper, 0.5 cm. thick.

Tube J is filled in the same manner with anhydrous calcium chloride (8 mesh) below, except that the wide end of the tube is fitted with a one-hole rubber stopper containing a short glass tube. The calcium chloride must have been previously treated with carbon dioxide as described in § 450.

Tube E is a glass stoppered U-tube with limbs 12 cm. long by 2 cm. outside diameter, equipped with glass braces to give it strength. To E, enough glass beads are added to fill the bend in the tube and sufficient saturated silver sulfate solution in 9 M sulfuric acid is then added to cover the beads. This solution is conveniently introduced by means of a small funnel. In the hollow part of the exit stopper a wad of glass wool or of cotton is placed. This serves to catch any spray which may form. A good grade of stop-cock lubricant is added to the glass stoppers

LEGEND

Soda Lime = 1

Calcium Chloride = 2

Cotton

AgSO4
H2SO4

INCHES
0 1 2 3 4 5 6 7 8 9 10

CENTIMETERS
0   4   8   12 16 20   25

Regulating Valve

Suction
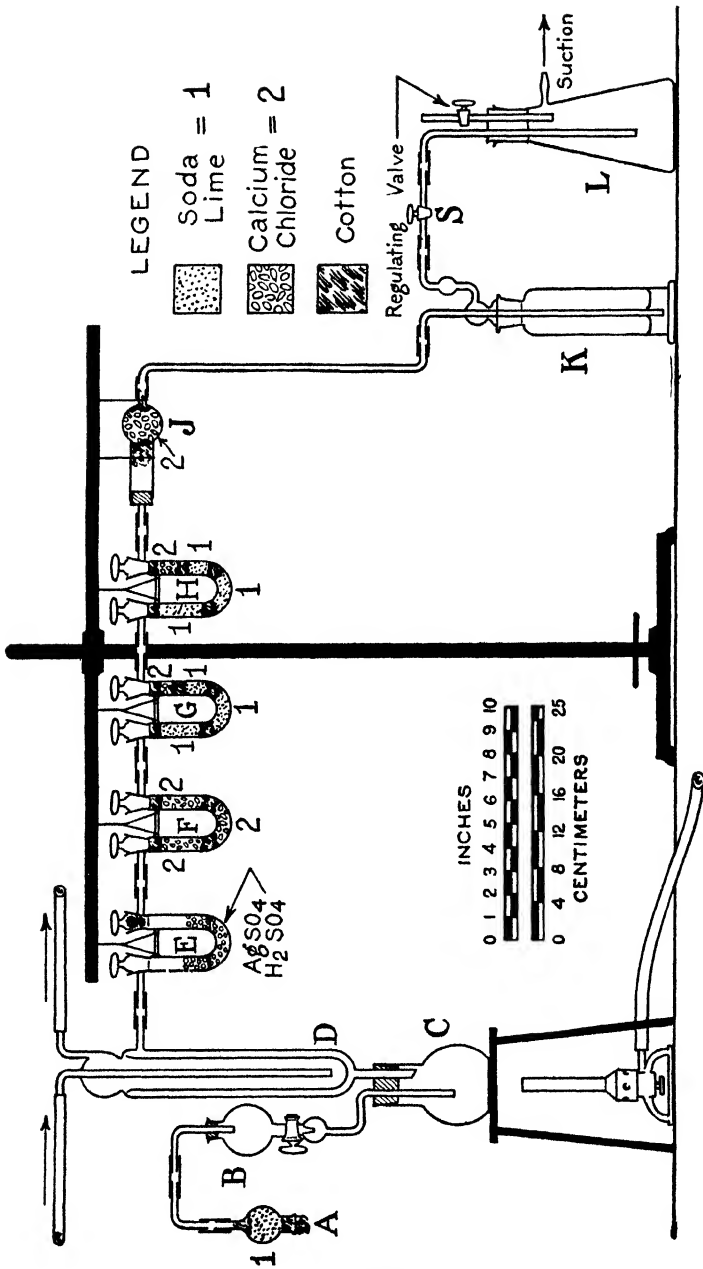
Fig. 87

Assembly for the Determination of Carbon Dioxide in Limestone

[544]

in sufficient amount to coat the ground surfaces and to make the joints gas tight. Any excess lubricant is then wiped away. This tube is designed to remove any hydrogen chloride which escapes the condenser.

Tube F, of the same type as E, is filled with calcium chloride (8 mesh) to catch the water vapor which is carried over from E. The calcium chloride used in F must have been previously treated with a dry stream of carbon dioxide and then of air, as described in § 450. The soda lime tubes, G and H, are prepared in the manner directed in § 450.

J is a guard tube similar to A but filled with anhydrous calcium chloride.

The bubble counter K contains 18 M sulfuric acid to the depth of about 3 cm.; the inlet tube of K, having an inside diameter of 0.5–0.7 cm., should be immersed to the depth of 1.6 cm.

L is a side-neck suction flask which is connected to a water pump and which serves as a water trap, should the pump flow back.

All rubber stoppers that are used should be of the very best grade of rubber, while the rubber tubing used for connecting the tubes should be of the heavy-walled pressure kind. Tubing 1.5 cm. outside diameter with 0.3 cm. bore is satisfactory. The connecting pieces should be about 4 cm. long.

An alternative arrangement is to fill F with dehydrite and to fill G and H each two thirds full of ascarite and one third full of dehydrite. The dehydrite in G and H is put at the exit end in each case and is separated from the ascarite by means of a layer of cotton. Half of J is filled with dehydrite and half with ascarite.

The apparatus and method described in this paragraph may be used for the determination of available carbon dioxide in baking powders, except that the dropping funnel should be filled with water instead of with hydrochloric acid.

454. Exercise No. 54. Determination of Carbon Dioxide in a Limestone. — Connect the apparatus as illustrated in Figure 87 and test it for any leaks as follows: Close the stop-cock on the dropping funnel which, of course, is lubricated, and open all the other stop-cocks so that they are in the "running" position. Turn on the water pump and draw a slight vacuum on the system,

then close the stop-cock S while the pump is still running. After S is closed, shut off the pump. The sulfuric acid in the bubble counter K will be depressed in the inner tube and elevated in the outer. If, at the end of three minutes, the meniscus in the inner tube has remained at the same position, the apparatus may be considered air-tight. If the levels should become equal, then the apparatus is leaking and each joint should be wired and coated with collodion. Do not reduce the pressure within the apparatus too much because the tubes and flasks are not designed to withstand great pressures and might shatter if care is not taken in this respect.

The Blank.—When the apparatus is found to be air-tight, turn all the stop-cocks to a "running position" and turn on the water pump so that the bubbles passing through the counter shall correspond to a rate of flow of about 30 ml. per minute. After air has been drawn through for fifteen minutes, turn off the suction, disconnect the tubes G and H, closing their stop-cocks at the same time. Wipe the tubes G and H carefully and weigh them one at a time, taking all the necessary precautions with respect to the charge on the tubes due to the wiping (see § 87). Reconnect the tubes G and H in position and draw air through the system for thirty minutes, and again determine the weights of G and H. These weights should not differ individually by more than 0.5 mg. from the preceding. If they do, the blank is unsatisfactory and the tubes must be again reconnected and the aspiration repeated.

Running the Unknown.—When a satisfactory blank has been obtained, connect the tubes G and H in their proper positions, and into the flask C transfer a weighed sample of the powdered limestone (about 1 g.), and add sufficient water to wet it. Open the stop-cocks of G and H, shut off the water pump, and close the stop-cock of the dropping funnel. Disconnect the guard tube A, and place in the dropping funnel 50 ml. of 6 M hydrochloric acid. Put the guard tube A back in place and gradually open the stop-cock of the dropping funnel so as to allow the hydrochloric acid to fall drop by drop upon the limestone (all the stop-cocks of the absorbing train must be turned in the "running position"). If the carbon dioxide is being evolved too

violently, cut down the rate at which the acid is being added, otherwise some of the carbon dioxide may escape being absorbed by the soda lime tubes. When all but a few milliliters of the acid has been added, close the stop-cock of the dropping funnel and gradually heat the solution in the flask C to boiling and keep it at this temperature for two or three minutes. Now start the suction pump and remove the flame from under the flask C and open the stop-cock of the dropping funnel. Suck air through the apparatus at the rate of 30 milliliters per minute for thirty minutes; at the end of this time, stop the suction pump and shut all the glass stoppers. Disconnect the tubes G and H. The absorption tubes become hot during the determination, due to the heat of reaction between the carbon dioxide and the soda lime. The water which is formed in the reaction, plus that aspirated away from the soda lime, is retained in the tube by means of calcium chloride placed over the soda lime. If the tubes G and H are still warm, allow them to cool to room temperature after wiping them free from any adhering dirt. Before weighing them, open the stop-cocks momentarily to equalize the inside pressure with that of the atmosphere. The gain in weight is carbon dioxide. From this weight, calculate the percentage of carbon dioxide in the sample.

455. Examples.

1. A sample of low carbon steel was analyzed for its carbon content as follows: First, a blank was run on the furnace; second, Bureau of Standards Steel No. 34 (C = 0.800%) was run as a control; third, the sample itself was run in duplicate. Soda Lime tube, A, was next the furnace, B followed A.

	A	B
Blank on Furnace		
Wt. of Soda Lime Tubes before run.....	39.3946 g.	45.2273 g.
Wt. of Soda Lime Tubes after 45 min.		
passing oxygen through furnace........	39.3949	45.2276
Bureau of Standards Steel No. 34		
Wt. of sample 2.001 g.		
Wt. of Soda Lime Tubes after combus-		
tion and sweeping out furnace 45 min.	39.4541	45.2279
Low Carbon Steel		
Determination 1. Wt. of sample 2.001 g.		
Wt. of Soda Lime Tubes after combus-		
tion and sweeping out furnace 45 min....	39.4704	45.2277

Low Carbon Steel — *Continued*   A   B

Determination 2. Wt. of sample 2.003 g.
Wt. of Soda Lime Tubes after combus-
tion and sweeping out furnace 45 min...   39.4869   45.2277

What % C was found for the Standard Steel No. 34 and for the Low
Carbon Steel, Determinations 1 and 2?

Ans.   0.805%.   0.225%.   0.222%.

2. A 2.0432 g. sample of steel was used in a determination of carbon by
means of the apparatus shown in Figure 86.   In the course of the combus-
tion, *G* gained 0.0160 g. and *H* gained 0.0002 g.   The blank obtained was
0.0004 g.   Calculate the per cent of total carbon in the steel.

3. In determining carbon dioxide in limestone with the apparatus shown
in Figure 87, the following data were obtained:

Blank.................... 0.0003 g.
Sample.................. 1.0647 g.
G before run............. 42.4526 g.
H before run............. 44.6491 g.
G after run............. 42.8639 g.
H after run.............. 44.6493 g.

Calculate the per cent of CO_2 in the sample.

4. When another portion of the sample used in Exercise 3 weighing
0.6119 g. was used in determining CaO the calcium was precipitated as
CaC_2O_4.   This precipitate was dissolved in sulfuric acid and was titrated
with 35.04 ml. of 0.05141 *M* $KMnO_4$ solution.   Calculate the CaO in
the sample.

5. Assuming that in the limestone of Exercises 3 and 4 all the CO_2 is
present as the carbonate of either calcium or magnesium and that all the
calcium and magnesium are present as carbonate calculate the per cent
of MgO in the sample.

CHAPTER XXIII

INTRODUCTION TO THE SYSTEMATIC ANALYSIS OF A SILICATE ROCK

456. General Considerations. — While it is general practice in many analyses, where the separation of constituent elements is unnecessary or can be avoided, to determine the various constituents on separate portions of the sample, there are, however, cases where it is necessary to separate and determine many of the constituents on one weighed portion. A conspicuous example in this regard is the analysis of earthy material commonly known as rock or of manufactured materials which are similar to rock in composition, namely, cements and slags.

A rock may be defined as a more or less complex mixture of the different mineral species which go to make up the earth's crust. Rocks may be classified, according to their composition, as silicate, carbonate, phosphate, and sulfate; or, according to their formation, as igneous and sedimentary, the latter comprising the sandstones, cherts and sinters, carbonates, slates and shales, and clays and soils. The average composition of rocks is given in Table 67, the data of which are taken from Clarke's "The Data of Geochemistry."[1]

Constituents frequently determined in rock analysis are SiO_2, Al_2O_3, total iron as Fe_2O_3, MgO, CaO, Na_2O, K_2O, H_2O at 110°, TiO_2, MnO, and P_2O_5. We shall limit our discussion to these constituents and refer the student for all further detail to the primary authority on rock analysis, W. F. Hillebrand, "The Analysis of Silicate and Carbonate Rocks" (reference given in § 11). At the very outset, it cannot be too strongly emphasized that a complete and accurate rock analysis requires extreme skill and care on the part of the analyst. The mere detail is intricate and taxes one's patience to the utmost. The beginner is warned

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[1] Frank W. Clarke, "The Data of Geochemistry," U. S. Geological Survey, Bulletin 695, 4th ed., Washington, 1920.

Table 67

A. Average composition of igneous rocks
B. Composite analysis of 78 shales
C. Composite analysis of 253 sandstones
D. Composite analysis of 345 limestones

	A	*B*	*C*	*D*
SiO_2	60.88%	58.38%	78.66%	5.19%
Al_2O_3	15.27	15.47	4.78	.81
Fe_2O_3	2.67	4.03	1.08	.54
FeO	3.49	2.46	.30	. . . .
MgO	3.82	2.45	1.17	7.90
CaO	4.92	3.12	5.52	42.61
Na_2O	3.43	1.31	.45	.05
K_2O	3.10	3.25	1.32	.33
H_2O at 110°	.49	1.34	.31	.21
H_2O above 110°	1.45	3.68	1.33	.56
TiO_2	.81	.65	.25	.06
ZrO_2	.023	. . . .	. . . .	. . . .
CO_2	.50	2.64	5.04	41.58
P_2O_5	.29	.17	.08	.04
S	.10	. . . .	. . . .	.09
Cl	.064	. . . .	Trace	.02
F	.10	. . . .	. . . .	. . . .
BaO	.104	.05	.05	None
SrO	.043	None	None	None
MnO	.10	Trace	Trace	.05
NiO	.026	. . . .	. . . .	. . . .
Cr_2O_3	.049	. . . .	. . . .	. . . .
V_2O_3	.026	. . . .	. . . .	. . . .
Li_2O	.011	Trace	Trace	Trace
SO_3	. . . .	.65	.07	.05
C, organic	. . . .	.81	. . . .	. . . .

that for even approximate determinations of the comparatively few constituents mentioned above, the analysis will be found trying and will require his greatest care. The example that we shall select will be the partial analysis of a silicate rock, because this is the most difficult of the various kinds of rocks to analyze and because the methods that apply to it apply with but slight

modification to the other kinds of rocks as well as to slags, cements and glass. In the prosecution of a rock analysis, evaporations should be made only in platinum or, less preferably, in porcelain vessels, while glassware should be avoided because of *its* solubility. The purity of reagents is an all-important matter, particularly the purity of those which are most frequently used, namely, sodium carbonate, ammonium hydroxide, ammonium chloride, and hydrochloric acid.

457. Exercise No. 55. Partial Analysis of Silicate Rock. — A material crushed so as to pass a sieve 70 meshes to the inch will serve for the analysis. The powder should be air-dried. The partial analysis for the constituents named in the preceding paragraph requires for the beginner in the neighborhood of ninety hours' time for completion. The results should add up to 99.75 %–100.5 %.

458. *Determination of Water at 110°.* — Weigh accurately into a previously weighed platinum or porcelain crucible about two grams of the rock powder and dry it for two hours in the electric oven at 110°; allow to cool in the desiccator and weigh. Repeat the heating and weighing until the loss in weight is constant. Report the loss in weight as water at 105°–110°. The loss in weight at 105°–110° is due mainly to hygroscopic water and also to essential water (water of constitution). In some cases, constant weight is difficult to obtain due to the slow loss of essential water. If extreme accuracy is not sought, the determination may be stopped when the weights of successive weighings differ by not more than 0.2–0.3 mg. For the determination of water above 110°, see W. F. Hillebrand, pp. 64–89 of the reference given in § 11.

459. *Decomposition of the Rock.* — Make an intimate mixture of 1 g. of rock powder with 5 or 6 g. of anhydrous sodium carbonate by stirring carefully in a weighed platinum crucible with a short glass stirring rod. Remove any rock powder from the rod by brushing with a camel's-hair brush. Cover the crucible and fuse, at first very carefully over a low Bunsen flame, then gradually over the full Bunsen flame, and finally over the full flame of a Meker burner until quiet fusion results and decomposition is complete. Sodium carbonate is used instead of the

more readily fusible equi-molecular mixture of sodium and potassium carbonates because the higher melting point of the sodium carbonate is a distinct advantage in the effective decomposition of some of the refractory rock constituents.   The heating with the Bunsen burner must be gradual because carbon dioxide is evolved as a result of the decomposition of the rock.   If a strong flame were used, the action might become violent and the evolution of carbon dioxide so rapid as to throw out of the crucible much of its contents.   The Meker burner, or in special cases the blast lamp, is employed to complete the decomposition, which is evidenced by the further evolution of carbon dioxide. At the end of the fusion, the result should appear as a viscous liquid, occasionally clear, though in general more or less turbid. The fusion must not be carried out in a muffle furnace because the platinum crucible appears to be unduly attacked under this condition.   While the melt is still liquid, grasp the crucible with a pair of tongs and rotate it so as to spread the molten mass around the inner walls of the crucible, and allow it to cool.

Other methods of decomposing rocks are by means of hydrochloric acid under pressure in a sealed tube; by fusion with boric oxide as the flux; and by treatment with hydrofluoric acid.   For a discussion of their relative merits, see W. F. Hillebrand, pp. 89–94, of reference given in § 11.

460. Determination of Silica. — To the cold crucible, add a little water and allow to stand for a few minutes.   If the fused mass can now be detached from the crucible, transfer it to a 500 ml. casserole and wash out the crucible, first with hot water and then with 6 M hydrochloric acid.   Wash off the crucible cover in the same manner.   If the fused mass cannot be removed from the crucible, place the crucible on its side in the casserole, cover with a watch-glass and add sufficient water to cover the crucible.   Allow to digest for some time and then add 6 M hydrochloric acid in excess and allow to digest until the mass is completely decomposed.   When the mass can be separated from the crucible, the latter is removed from the casserole, washed with hot water and any film of silica removed by wiping with a small piece of ashless filter paper.   This paper is kept to be added to the main portion of the silica to be obtained later.

Place the casserole on a steam-plate and heat. When the liberation of carbon dioxide ceases, remove the watch-glass and wash the solution from its under side into the casserole and continue the evaporation after placing some glass bends around the edge of the casserole to support the watch-glass. The solution may be further protected from dust by supporting a large inverted funnel over it by means of a ring stand and clamp. Evaporate the solution to dryness on the steam-plate. For this evaporation, only platinum or porcelain should be used. Glassware should be avoided because of its solubility. If a platinum dish is used, a small amount of it (1–2 mg. or possibly more) passes into solution, especially if much ferric ion is present, according to the following equation:

$$2\ Fe^{+++} + Pt^{\circ} \rightarrow 2\ Fe^{++} + Pt^{++}.$$
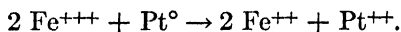
Also some platinum is brought into solution by the oxidizing action of manganates, vanadates, and chromates in the hydrochloric acid solution during the evaporation. For example, in the case of manganate, we have

$$MnO_4^- + 8\ H^+ + 8\ Cl^- + 2\ Pt^{\circ} \rightarrow Mn^{++} + 4\ H_2O + 2\ PtCl_4^=.$$
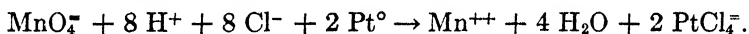
Place the casserole in an oven at 110°–120°, or on a hot-plate at this temperature, for twenty minutes to dehydrate the silica. Heating the silica residue to 110°–120° is done, not to increase the amount of insoluble silica, but rather to aid the subsequent filtration and washing. The residue is not heated higher than 120° because the amount of insoluble impurity in the silica increases with increase of temperature of dehydration. Moisten the residue from the evaporation with a few milliliters of water, then with 10 ml. of 12 M hydrochloric acid, turning the casserole so that the hydrochloric acid comes in contact with all portions of the residue. Add 20–30 ml. of hot water and heat the casserole on the steam-plate for a few minutes, stirring every now and then until all soluble salts are dissolved; then allow the silica to settle and decant the solution through a 12 cm. filter paper. Add 2–3 ml. of 12 M hydrochloric acid to the silica in the casserole, then 10–20 ml. of hot water, decant through the filter and repeat until the addition of hydrochloric acid to the residue in the casserole

gives no yellow color due to iron. Transfer the silica to the filter and wash alternately with cold water and cold 3 M hydrochloric acid, and finally with hot water until all soluble salts are removed from the filter. The thin film of silica which adheres to the casserole need not be removed at this time. The filtrate is returned to the casserole and evaporated to dryness on the steam-plate as before. Treat the residue exactly as before and filter through a 7 cm. filter paper, removing all of the silica from the casserole. It is impossible to obtain all of the silica by one evaporation and dehydration. At least two evaporations and dehydrations with intervening filtrations are necessary to remove the major portion of the silica. The amount of silica passing into the filtrate after the first evaporation and dehydration is from 1–3% of the total amount present. The solubility of the silica after the first dehydration is probably due to the slight amphoteric character of silicic acid, although certain salts, such as sodium chloride and magnesium chloride, have a marked effect in increasing its solubility. If the volume of the filtrate is greater than 300 ml., evaporate it in a casserole to about 300 ml. so that it will be ready for the operation of § 461 by the time the remaining operations given in this paragraph are completed. Remove as completely as possible the last thin film of silica which adheres to the porcelain by wiping the inside of the casserole with a small piece of ashless filter paper; add this paper to the main portion of the silica. Ignite the silica precipitates in a weighed platinum crucible as described in § 37. In the ignition of silica, in order to dehydrate it completely, it is necessary to heat the crucible to the highest temperature of the Meker burner for at least thirty minutes after all the carbon of the filter paper has been oxidized. After constant weight has been secured, moisten the silica with water, add two drops of 18 M sulfuric acid and then 10–15 ml. of hydrofluoric acid. Evaporate to dryness in an air-bath as described in § 20, and ignite the residue over a Bunsen burner. The silica is removed by this treatment due to the formation and volatilization of silicon tetrafluoride, SiF_4. Since the ignited silica is never pure, there is always a weighable residue after evaporation with hydrofluoric acid. This residue consists of aluminum oxide, ferric oxide and titanium phos-

phate. The loss in weight represents the major portion of the silica present in the sample, though a small amount still remains to be recovered from the iron and aluminum oxides to be obtained later. The crucible with the slight residue from the silica determination is set aside until the iron and aluminum precipitate is ready for ignition; the ignition of this latter precipitate is then made in this crucible.

Silica is occasionally introduced into the analysis by the porcelain ware used and by the sodium carbonate. The sodium carbonate used is rarely pure. Even the purest samples show foreign matter to the extent of 0.01%. This consists mainly of silica, alumina, and calcium oxide.

461. Determination of the Combined Weights of Al_2O_3, Fe_2O_3, $TiPO_4$, Mn_3O_4, etc. — In the following separation, the manganese is thrown down as manganese dioxide along with the hydroxides of aluminum, iron, etc., and, if phosphate is present, with the phosphates of aluminum, iron and calcium. This handling of the manganese is not altogether satisfactory as some of the manganese remains in solution and distributes itself later with the calcium and magnesium. There are several alternative methods of handling the manganese, but all of these are attended with certain objections, for the details of which the student must consult Hillebrand, p. 134 *et seq.* of reference given in § 11.

The filtrate from the dehydration should have a volume of about 300 ml. and a concentration of ammonium chloride of at least 0.5 M. This concentration of ammonium chloride is necessary to prevent the precipitation of magnesium hydroxide. Add a few drops of methyl red solution to the filtrate, heat just to boiling and then add carefully 3 M ammonium hydroxide, drop by drop, until the color of the solution changes to a distinct yellow. If much iron is present, the end point is still easily determined because ferric hydroxide precipitates before the solution is alkaline to methyl red, and upon its settling out, the color of the supernatant liquid is easily seen and may be brought to the proper tint by the addition of more ammonium hydroxide, or any large excess of base may be removed by the addition of 3 M hydrochloric acid. By this method, the solution is given a pH of 7 with the result that aluminum ion is quantitatively precipi-

tated as hydroxide.[2]   To the faintly alkaline solution containing the precipitated hydroxides of aluminum, iron, etc., add 10–15 ml. of bromine water and let stand for about fifteen minutes; the manganous ion is oxidized to hydrated manganese dioxide $MnO_2 \cdot H_2O$ which precipitates out.   Decant the solution through a 12 cm. filter paper.   A filter paper of this size will accommodate an amount of precipitate corresponding to about 200 mg. of mixed oxides, but will not accommodate much more.   Wash the precipitate once or twice by decantation, using hot water.   Remove the filter paper from the funnel and place it in the beaker in which the first precipitation was made.   Add a little 12 M hydrochloric acid and, with a stirring rod, break up the filter paper into a pulp of paper fibre.   The maceration of the filter paper serves several purposes.   Its presence makes more thorough washing of the precipitated hydroxides possible, and in their subsequent ignition it gives a powdery residue.   This fine state of division of the ignited residue permits the re-oxidation of any reduced oxide to take place quickly, and also shortens the time for the re-solution of the oxides.   When the maceration of the filter paper is omitted, the residue after ignition is lumpy and hard, while any iron oxide that has been reduced to the ferrous state is with difficulty oxidized to the ferric state.

Add a little water and a few drops of sulfurous acid to dissolve any manganese dioxide and turn the beaker so that the ferric hydroxide adhering to the sides of the beaker is all dissolved. When the precipitate has dissolved, dilute the solution to about 300 ml., heat to boiling and precipitate as before with 3 M ammonium hydroxide until just alkaline to methyl red.   Double precipitations must be employed to separate aluminum, iron, titanium, phosphorus, chromium, etc., from calcium and magnesium.   As previously mentioned, some of the manganese will stay in solution with the calcium and magnesium, while most of it will go with the aluminum, iron, etc.   For extreme accuracy, rocks high in magnesium require three precipitations.

Filter the solution through a 12 cm. filter paper and wash the precipitate with 0.2 M ammonium nitrate solution.   It is important to add the wash water in such a manner that the precipitate

[2] Blum, *J. Am. Chem. Soc.*, **38**, 1282 (1916).

will be thoroughly stirred from the bottom of the filter paper. When the precipitate is washed free from chlorides, add the filtrate to that from the first precipitation and evaporate to about 250 ml. for the determination of the calcium as described in § 465. If, during this evaporation, aluminum or ferric hydroxides separate, remove them by filtration through a small filter paper, wash and add to the main precipitate obtained above. Now ignite this precipitate in the platinum crucible containing the residue from the silica determination in § 460, finally subjecting it to the full flame of the Meker burner for about thirty minutes; then cool in the desiccator and weigh. The ignited precipitate is sometimes reported as "Combined Oxides" without any further work being done upon it.

462. Determination of Total Iron in the Combined Oxides. — Mix the combined oxides of aluminum, iron, etc., in the platinum crucible with 7–8 g. of potassium pyrosulfate which, because it is rarely free of iron, must have been previously tested for the presence of iron. Fuse carefully with the cover on the crucible at a temperature of about 300°, or just above the point where fumes of sulfur trioxide come off, until complete solution of the oxides results. There should be no dark particles floating about in the red-hot flux at the bottom of the crucible. A pyrosulfate fusion is necessary in order to dissolve the oxides, because after ignition the oxides dissolve in acids slowly and with great difficulty. Allow the fusion to cool, turning the crucible so that the fused mass is spread around the inner walls of the crucible. Fill the cold crucible about three-quarters full with 18 M sulfuric acid and heat very carefully on the steam-plate, stirring with a short glass rod which is left in the crucible as a stirring rod. The mass can in this way be broken into a fine-grained precipitate, most of which dissolves in the hot acid. Place on the hot-plate and continue the heating until dense fumes of sulfur trioxide are liberated freely. Platinum is introduced into the analysis through the potassium pyrosulfate fusion and the treatment of it with sulfuric acid. For every gram of potassium pyrosulfate used, about 0.5 mg. of platinum is dissolved from the crucible per hour, while 1 ml. of hot (280°–300°) 18 M sulfuric acid may dissolve as much as 0.4 mg. of platinum in ten minutes. It is important,

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therefore, not to prolong unduly the treatments with the pyro-sulfate and the sulfuric acid.

Allow the crucible and contents to cool and transfer to a beaker. Add 100 ml. of cold water and heat. Remove the crucible and wash the solution from it back into the beaker. After heating this solution for a short time, everything should dissolve except a few flakes of silica. Filter through a very small filter paper and wash with 0.5 M sulfuric acid until free of iron. Ignite in a platinum crucible and weigh (this crucible need not be weighed empty). Add a drop of 9 M sulfuric acid and a few drops of hydrofluoric acid and evaporate and ignite. The loss in weight is silica. Add this to the silica previously found and calculate the percentage of the total and report as silica. Fuse the slight residue remaining in the crucible after the removal of the silica, mentioned above, with a little potassium pyrosulfate; dissolve by adding a little 9 M sulfuric acid and water, and heating; then add the solution to the main solution of the combined oxides.

Adjust the concentration of free sulfuric acid in the solution of the combined oxides so that it shall be between 0.3 and 0.5 M, and pass in hydrogen sulfide. In the reduction of the ferric ion, the concentration of sulfuric acid should be 0.3–0.5 M, because the reduction is dependent upon the concentration of sulfide ion and this, in turn, upon the concentration of hydrogen ion. Any increase in the latter above the limits mentioned results in a dimi-nution of the former to an extent that the reduction $Fe^{+++} \rightarrow Fe^{++}$ is not quantitative. See § 344. Heat the solution and pass in more hydrogen sulfide and finally allow to cool while the hydrogen sulfide is still passing into the solution. Hydrogen sulfide is used in preference to stannous chloride or zinc for the reduction of ferric ion because titanium and vanadium are almost invariably present in a rock, and the hydrogen sulfide does not reduce titanic ion and only reduces vanadate ion to vanadyl ion, thus permitting a correction for the vanadium in the subsequent titration with permanganate. If either stannous chloride or zinc is used as the reducing agent, this correction is impossible, as shown in § 338.

After the platinum sulfide and sulfur precipitate has collected, filter into a 500 ml. Erlenmeyer flask, wash the filter paper free from iron with 0.5 M sulfuric acid, and again pass hydrogen sulfide

into the solution. Disconnect the hydrogen sulfide generator and connect a carbon dioxide generator [3] to the inlet tube. While passing an adequate current of carbon dioxide through the solution, heat the flask to boiling and continue until no more hydrogen sulfide is carried out by the carbon dioxide, as shown by testing the gas issuing from the delivery tube of the flask with filter paper which has been moistened with a solution containing lead acetate. While the carbon dioxide is still passing through the solution, allow the latter to cool to room temperature and titrate at once with standard potassium permanganate solution. From the result, calculate the percentage of total iron in the rock as Fe_2O_3.

Phosphorus cannot be determined in the combined oxides because fusion of the oxides with pyrosulfate and fuming of the melt with sulfuric acid volatilizes some of the phosphorus.

463. Determination of Titanium. — If titanium is to be determined, evaporate the solution of the combined oxides after titration with permanganate to less than 100 ml., if the percentage of TiO_2 is less than one per cent; for each additional per cent, the volume is increased by 100 ml. Now transfer the solution to a graduated flask having a capacity of 100–200 ml., or more, and add enough hydrogen peroxide to peroxidize the titanium fully. Fill the flask with water to the mark, shake well, and determine the titanium colorimetrically. For detailed directions, see W. F. Hillebrand, p. 155 of reference given in § 11.

464. Determination of Aluminum. — The aluminum in the sample is found by difference as follows: From the weight of the combined oxides, deduct the weight of the Fe_2O_3 found, also the weight of any of the other oxides known to be present and which have been determined, and calculate the result to per cent of the sample. Report this result as "$Al_2O_3(TiO_2, P_2O_5$, etc.) by difference," putting in parentheses those constituents known to be present but which have not been determined individually.

[3] Compressed carbon dioxide contained in a tank, which has a suitable reducing valve, is admirably adapted for this purpose. If the carbon dioxide is generated from marble by means of hydrochloric acid, care must be taken to free the carbon dioxide of the hydrochloric acid which it entrains. (See § 453.)

Since the Al_2O_3 is determined by difference, the errors involved in the determinations of the other oxides known to be present in the combined oxides fall upon the Al_2O_3, unless the errors happen to balance each other.

465. *Determination of Calcium.* — Concentrate the filtrate from the precipitation of the aluminum and iron to a volume of about 200 ml., heat to boiling and treat with an amount of 0.25 M ammonium oxalate solution equivalent to all the calcium and magnesium present plus an excess of ten per cent of this amount. Add 3 M ammonium hydroxide until the solution is slightly alkaline and allow to stand on the hot-plate for about an hour, or until the crystals of calcium oxalate are large enough to be retained by the filter paper. If much magnesium is present, the precipitation of the calcium oxalate is delayed. This peculiar behavior is probably due to the fact that magnesium ion forms a complex with oxalate ion and, consequently, the first additions of $C_2O_4^-$ are removed by Mg^{++} to form this complex. It is only after most of the Mg^{++} has been taken care of in this way that the solubility product of CaC_2O_4 is exceeded. Digestion of the calcium oxalate should not be too prolonged because MgC_2O_4 settles out upon the CaC_2O_4 on standing, especially if the amount of magnesium is large. MgC_2O_4, however, easily forms supersaturated solutions and, if agitation is avoided, it tends to remain in that condition. Decant the solution through a 7 ml. filter paper, leaving as much of the precipitate as possible in the beaker. Place the beaker containing the precipitate under the funnel, and pour a little hot 3 M hydrochloric acid through the filter to dissolve any precipitate that may have been transferred while decanting the solution. Wash the paper with hot water until free from chloride ion, then heat the beaker with its precipitate and solution, adding enough 3 M hydrochloric acid to effect solution of the precipitate. Dilute to about 150 ml., add 2–3 ml. of 0.25 M ammonium oxalate solution, then make the solution slightly alkaline by adding 3 M ammonium hydroxide slowly, drop by drop. Double precipitation of the calcium oxalate is necessary because this precipitate drags down magnesium oxalate to the extent of 0.1 to 0.2 %. Some sodium oxalate is also dragged down in small amounts. Digest the precipitate as in the first precipitation and

filter through a 7 ml. filter paper. Wash with hot water, adding a drop of 0.25 *M* ammonium oxalate each time the funnel is filled. Combine the filtrates containing the magnesium, and concentrate by evaporation to a volume of about 100 ml. and reserve for the determination of magnesium in § 466. Transfer the filter paper and its precipitate to a platinum crucible that has been weighed with its cover. Ignite gently by first charring the filter paper, then ignite strongly over the Meker burner.

The conversion of CaC_2O_4 to CaO does not require much time nor a very high temperature.[4] While cooling, the calcium oxide should not be left more than thirty minutes in the desiccator, because it gains in weight, due probably to absorption of gases such as CO_2, H_2O or SO_3 which may be present.

Weigh the crucible and calcium oxide quickly and with the cover of the crucible in place so that the amount of moisture and carbon dioxide absorbed from the air will be negligible. Ignite to constant weight and calculate the percentage of calcium as CaO. The calcium oxide obtained will contain strontium oxide because strontium is almost invariably present. If barium is present in small amounts (it is rarely absent), very little or no barium oxide will be found with the calcium oxide when a double precipitation is employed.

Other methods for determining the calcium after precipitation as CaC_2O_4 are: Solution of the CaC_2O_4 in dilute sulfuric acid and titration of the $C_2O_4^=$ with permanganate; decomposition of the oxalate into carbonate and weighing as $CaCO_3$ (poor); conversion of the oxalate into $CaSO_4$ or CaF_2 and weighing as such. See Chapter XII.

466. *Determination of Magnesium.* — Before beginning the determination of magnesium, it is advisable to re-read Chapters XI and XII, especially those parts which deal with the precipitation and handling of $MgNH_4PO_4 \cdot 6H_2O$, and the precautions which must be observed. Concentrate the filtrate from the calcium oxalate precipitation to a volume of 75–100 ml. If ammonium salts are present to the extent that they crystallize

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[4] Hillebrand has shown that a good Bunsen burner will quantitatively convert 3 g. of $CaCO_3$ to CaO in one hour. Hillebrand, p. 142 of reference given in § 11.

from the solution when the latter cools to room temperature, the greater portion of them may be removed by adding 20–25 ml. portions of 16 M nitric acid and continuing the evaporation. There must be enough ammonium salts present to prevent the precipitation of magnesium hydroxide by means of ammonium hydroxide, and yet the concentration of ammonium salts should not exceed 0.4 M because larger concentrations hinder the subsequent precipitation of $MgNH_4PO_4 \cdot 6H_2O$ and also affect the composition of the precipitate. To the concentrated solution, add about 5 ml. of 3 M hydrochloric acid and then 3 M ammonium hydroxide until the solution is alkaline (odor of ammonia). If a precipitate of magnesium hydroxide forms, repeat the addition of hydrochloric acid and of ammonium hydroxide until the solution can be made alkaline without the formation of a precipitate. Next make the alkaline solution slightly acid to methyl orange by means of 3 M hydrochloric acid, and then add 0.25 M di-sodium phosphate solution until it is present in forty per cent excess over the amount theoretically corresponding to the amount of magnesium present. See that the temperature of the solution is not over 30°, and then add from a pipette or burette, drop by drop, 15 M ammonium hydroxide until the solution is faintly alkaline, and then enough more to make the final concentration of ammonium hydroxide in the solution 1.5 M; allow to stand at room temperature for four hours. The precipitate of magnesium ammonium phosphate hexahydrate, which will carry about 0.5 mg. of CaO as $Ca_3(PO_4)_2$, is neither weighed directly nor ignited to the pyrophosphate. Filter through a 7 cm. filter paper and wash two or three times with 1.5 M ammonium hydroxide solution, rejecting the filtrate and washings. Dissolve the precipitate through the filter paper by means of 3 M hydrochloric acid, taking care not to use more of the acid than is really needed, and wash the filter paper free of chloride ion by means of distilled water. Treat the solution containing the dissolved magnesium ammonium phosphate and having a volume of about 40 ml. with 0.5–1 ml. of 0.25 M di-sodium hydrogen phosphate solution, and then with 15 M ammonium hydroxide solution, added dropwise, until the solution is faintly alkaline, and then with enough more to make the final concentration of ammonium hydroxide

1.5 M.   After this, allow it to stand at room temperature for four hours.   In rock analysis, it is always desirable to run a double precipitation for magnesium.   The re-precipitated magnesium ammonium phosphate will be contaminated, as before, with about 0.5 mg. of CaO as $Ca_3(PO_4)_2$.   It may also be contaminated with manganese as $MnNH_4PO_4 \cdot H_2O$, if this element was not previously removed with the combined oxides or otherwise, and by barium phosphate and calcium phosphate.   If a double pre-cipitation of the magnesium is employed and the amount of barium originally present was small, no barium will contaminate the precipitate.

Filter the solution through a 7 cm. filter paper and wash with 1.5 M ammonium hydroxide solution until free from chloride ion, after which ignite it to magnesium pyrophosphate in a platinum or, less preferably, in a porcelain crucible by means of a Meker burner, after charring the filter paper in the usual manner.   Observe the precautions in this regard mentioned in § 226.   After ignition of the precipitate, the calcium will still be present as $Ca_3(PO_4)_2$, and in precise work it must be determined and a correction applied accordingly (see Hillebrand, p. 152 of reference given in § 11).   Calculate the percentage of magnesium as MgO.

467.   The J. Lawrence Smith Method of Decomposition of Sample, Prior to the Determination of Potassium and Sodium. — For the determination of potassium and sodium, a separate sample is taken and decomposed by the fusion method of J. Lawrence Smith.[5]   The details of the method are as follows: Weigh out about 0.5 g. of the rock powder and transfer it to an agate mortar.   Very carefully grind this powder until no granular material can be felt under the pestle.   Add 0.5 g. of ammonium chloride ("Analyzed" grade)[6] and grind together.   Weigh out from 4–6 g. of calcium carbonate ("Analyzed" grade) and add nearly all of this to the mixture in the agate mortar.   Grind

[5] J. Lawrence Smith, *Am. J. Sci.* (2) **50,** 269 (1871).

[6] "Analyzed" grades of ammonium chloride and calcium carbonate should be used in order to insure that these reagents be as free as possible from po-tassium and sodium.   For extreme accuracy, a blank should be run on these two reagents.

together until thoroughly mixed. Very carefully transfer this mixture to a platinum crucible, preferably of the J. Lawrence Smith type [7] which, due to its depth, lessens the danger of loss of alkalies by volatilization; use the remaining portion of the calcium carbonate to wash the powder from the mortar to the crucible. Place the cover on the crucible and see that it fits tightly. Place the crucible in a hole in an asbestos board in such a manner that about one-half of the crucible projects through the hole. Heat very gently, with a low flame of the Bunsen burner, for ten to fifteen minutes. As soon as the odor of ammonia is no longer perceptible, gradually increase the flame until the crucible is finally treated with the full flame of the burner. The asbestos board will protect the upper half of the crucible from the flame so that it will be at a temperature below that at which sodium chloride and potassium chloride are volatile; as a further security that the upper part of the crucible shall not get too hot, the lid of the crucible may be kept filled with water. Continue the heating with the full flame of the Bunsen burner for about one hour. At the end of this time, the contents of the crucible should be sintered together in the form of a cake, but not fused. If fusion has occurred, the determination must be repeated, using a larger portion of calcium carbonate in the mixture. The reactions taking place during the decomposition may be written as follows, sodium and lithium behaving the same as potassium:

1. $CaCO_3 + \triangle \rightarrow CaO + CO_2$
2. $CaO + 2KAlSi_3O_8 + \triangle \rightarrow Ca(AlSi_3O_8)_2 + K_2O$
3. $CaO + 2NH_4Cl + \triangle \rightarrow CaCl_2 + 2NH_3 + H_2O$
4. $K_2O + 2NH_4Cl + \triangle \rightarrow 2KCl + 2NH_3 + H_2O$

This method, compared with other methods of decomposition such as treatment of the rock powder with hydrofluoric and sulfuric acids, or fusion of the rock powder with the oxides of boron, lead, or bismuth, possesses the marked advantage that

[7] J. Lawrence Smith used a special form of crucible which since bears his name and which is always used for precise work. It is about 8.2 cm. long with an inside diameter of 1.9 cm., being made of extra heavy platinum and carrying a closely fitting cap. For student purposes, the ordinary crucible, used as described above, works fairly well.

magnesium is completely eliminated at the beginning of the analysis.

468. *Determination of Combined Chlorides.* — Transfer the sintered cake to a 300 ml. casserole and treat with about 50 ml. of water. Heat and break up the lumps with the end of a stirring rod. Wash by decantation, using successive small portions of hot water and heating and breaking up any lumps that remain. Receive the filtrate in a casserole, and wash the residue well with hot water. Before going any further with the filtrate, test the residue to see if the decomposition of the sample has been complete. If the decomposition has been complete, the residue should dissolve completely in 3 M hydrochloric acid. Some silicic acid may separate during this acid treatment, but there should be no particles of the original rock powder left; if there are any particles left, they will be readily distinguishable and the determination must begin anew; if no particles are present, then the hydrochloric acid solution of the residue may be discarded, and the analysis continued on the filtrate from the sintered cake.

Assuming that the decomposition has been satisfactory, concentrate the filtrate from the sintered cake, if necessary, until its volume is not over 200 ml., heat to 90°–95° and then precipitate the calcium as calcium carbonate by means of 0.25 M ammonium carbonate, making the solution slightly alkaline by means of 3 M ammonium hydroxide. Digest until the precipitate is granular and settles readily. Decant through a 7 cm. filter paper and wash several times by decantation, using hot water, and receiving the filtrate in a large platinum or fused silica evaporating dish. Place the dish on a water-bath or steam-plate to evaporate, and place the casserole in which the precipitation was made under the funnel holding the precipitate. Dissolve the precipitate through the filter paper by pouring over it successive small portions of 3 M hydrochloric acid. Wash the filter paper with hot water. Re-precipitate the calcium from this solution as calcium carbonate in the manner described above. The double precipitation of calcium as carbonate is necessary because some potassium and sodium are carried down in the first precipitation. Filter and wash with hot water as above, collecting the filtrate in a small beaker. From time to time as the original filtrate in

the evaporating dish evaporates, add this second filtrate to it until finally the whole of the two filtrates from the calcium carbonate precipitations is contained in the evaporating dish. Continue the evaporation until the residue is perfectly dry. Very carefully ignite the residue in the evaporating dish to drive off all ammonium salts. Dissolve the residue in about 5 ml. of water,[8] add a few drops of 3 M ammonium hydroxide and heat to 60°–70°; add, a few drops at a time, 0.25 M ammonium oxalate solution until in slight excess. Cover with a watch-glass and heat on a water-bath or steam-plate until the precipitate settles readily. Ammonium oxalate is used to remove the final traces of calcium, because calcium oxalate is very much more insoluble than the carbonate. Filter the solution, through a very small filter paper and funnel, into a 50 ml. platinum or fused silica evaporating dish. Wash carefully with successive small portions of hot water, so that the washing will be thorough but the volume of wash water small. Evaporate to dryness and then dry in the oven at 115°–120°. Ignite very carefully to drive off ammonium salts and oxidize organic matter. The temperature must be below the point at which the chlorides fuse so as to avoid any loss of them through volatilization. Cool and moisten with a few drops of 3 M hydrochloric acid, and again evaporate and ignite as above. Cool and weigh; this gives the weight of the combined chlorides plus a few tenths of a milligram of impurity in the form of silica. Dissolve the salts in a little water and filter through a very small filter paper into another 40 ml. evaporating dish. Wash the filter paper thoroughly with hot water, and then place it in the original evaporating dish in which the combined chlorides were weighed. Dry and ignite the filter paper. Allow the dish to cool and then weigh it. From this weight and the previous weight of the combined chlorides plus impurity, the weight of the combined chlorides is obtained.

[8] If the rock contains sulfur in any appreciable amount, this element must be separated at this juncture, otherwise the weight of the combined chlorides of potassium and sodium subsequently will be slightly high, due to its presence as sulfate. It may be removed by the addition of a few drops of 0.25 M barium chloride solution before the final removal of the calcium as calcium oxalate. The excess barium ion is removed by ammonium carbonate and the small trace of calcium is then removed as oxalate, as described in the text.

469. *Separation of Potassium by Precipitation as Potassium Chlorplatinate.* — Evaporate the solution of the combined chlorides to 10–15 ml. and carefully add an excess of 0 2 M chlorplatinic acid. The dilution of the chlorides must be such that any precipitate of potassium or sodium chlorplatinate that separates at this point will dissolve on heating on the water-bath. If it does not dissolve, add a little water until it does. Evaporate this solution until the residue will just solidify when the solution cools. It must not be heated until all the water has been driven off, otherwise some of the sodium chlorplatinate is rendered insoluble by being converted from $Na_2PtCl_6 \cdot 6H_2O$ to the anhydrous material, Na_2PtCl_6. Add 10–15 ml. of 80% (by volume) alcohol to the residue, stir with a stirring rod and allow to stand for a few minutes. The solution must be strongly colored yellow by the excess of chlorplatinic acid; if it is not, add a few milliliters more of the latter. Filter through a 7 cm. filter paper, being careful to keep most of the precipitate back in the evaporating dish. Wash by decantation with successive small portions of 80% (by volume) alcohol until the residue is free of the excess chlorplatinic acid and of sodium and lithium chlorplatinates. The separation of sodium chlorplatinate $Na_2PtCl_6 \cdot 6H_2O$ from potassium chlorplatinate K_2PtCl_6 depends upon the solubility of the former in 80% (by volume) alcohol and the insolubility of the latter. Lithium, if present, will be in the form of $Li_2PtCl_6 \cdot 6H_2O$, which is soluble in the 80% alcohol. All ammonium salts must be absent because they would give ammonium chlorplatinate $(NH_4)_2PtCl_6$, which is insoluble in 80% alcohol. The potassium chlorplatinate which remains may now be treated in either one of two ways, of which *Method A*, in which the amount of platinum in the potassium chlorplatinate is determined, is preferable to *Method B*, in which the potassium chlorplatinate itself is weighed. The reason for this preference is found in the fact that the composition of the precipitate, K_2PtCl_6, is somewhat variable, in that the ratio of Cl to the other two elements is not constant, while the ratio of Pt to K is constant (see Mellor, p. 234 of reference given in § 11).

470. *Method A for the Determination of Potassium.* — Place the evaporating dish containing the major portion of the potassium chlorplatinate under the funnel through which the

filtration was made, and dissolve through the filter, by means of hot water, whatever crystals of precipitate might be there; wash. Add hot water to the main portion of the precipitate, transferring it to a 250 ml. beaker, finally adding enough hot water, say 150 ml., to dissolve the precipitate. Now add enough 12 M hydrochloric acid to make the concentration of the acid about 0.5 M, and add about 0.5 g. of metallic magnesium, or more if necessary, in the form of powder or ribbon so that the platinum in the potassium chlorplatinate shall be precipitated as metallic platinum. This reduction should be effected either in a glass or porcelain dish, never in a platinum dish, because the finely divided platinum resulting from the reduction sticks to every scratch in the platinum dish and cannot be removed. Filter off the platinum on filter paper, wash, ignite, and weigh as Pt. From this weight the amount of K_2O can be readily calculated.

471. Method B for the Determination of Potassium. — Place the evaporating dish containing the major portion of the potassium chlorplatinate under the funnel through which the filtration was made and dissolve through the filter paper, by means of hot water, whatever crystals of precipitate might be there; wash. Evaporate the potassium chlorplatinate and washings to dryness on the steam-plate or water-bath. Cover the dish with a watch-glass supported by glass bends and transfer to an electric oven and dry to constant weight at 125°. In this drying, the potassium chlorplatinate decrepitates, hence the necessity of covering the dish. After constant weight has been obtained, dissolve the potassium chlor-platinate by means of hot water, dry the dish at 125° as before, cool and weigh. The difference in weight gives the weight of K_2PtCl_6, and from this weight the amount of K_2O can be calculated.

472. Determination of Potassium by Precipitation as Potassium Perchlorate. — Instead of precipitating the potassium by means of chlorplatinic acid, which is rather expensive, the relatively inexpensive perchloric acid can be used, although the results with the latter reagent are not so precise. The procedure is as follows: After removing the calcium and ammonium salts, and sulfate, as described in § 468 for the chlorplatinic acid pre-cipitation, weigh the combined chlorides and then dissolve them

in the same dish in a small amount of water.   Add several milli-
liters of 3 M perchloric acid and evaporate the solution to dense
fumes of perchloric acid by means of an electric hot-plate or a
small free flame.   This treatment serves to convert the chlorides
into perchlorates, thus,

$$KCl + HClO_4 \rightarrow KClO_4 + HCl,$$
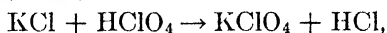
the hydrochloric acid being volatilized.[9]   Fume a short while but
not sufficiently long to bring the residue to dryness, since this
would cause one salt to become encrusted with the other, and
thereby bring about subsequent difficulty in separating the sodium
perchlorate from the potassium perchlorate by extraction with
alcohol.   Allow the residue to cool, add 5 ml. of water to dissolve
the salts, then 2–3 ml. of 3 M perchloric acid, and evaporate to
fumes again in order to make sure of the conversion of the chlorides
to perchlorates.   Cause the residue to cool to $10°–15°$, add 10 ml.
of absolute alcohol containing 0.2% of perchloric acid [10] and let
stand ten minutes, meanwhile breaking up any small lumps by
means of a blunt glass rod.   The residue, after evaporation to
fumes of perchloric acid, must not be allowed to stand any length
of time before adding the absolute alcohol mixture, because
perchloric acid is hygroscopic as is also the absolute alcohol.
The introduction of any water increases the solubility of $KClO_4$.[11]
Decant the supernatant liquid through a weighed Gooch crucible
which has previously been dried at $125°–130°$, leaving most of
the precipitate in the dish.   Add 5 ml. of water to the precipitate
and heat gently until it dissolves; then add 2 ml. of 3 M perchloric
acid and evaporate to fumes.   Again cause the residue to cool
to $10°–15°$, add 10 ml. of the absolute alcohol containing 0.2%
of perchloric acid and let stand for ten minutes, meanwhile
breaking up any small lumps.   Decant the supernatant solution
through the same Gooch crucible as before, and then transfer
the residue to the crucible, using the least amount possible of the

[9] If the potassium and sodium were present as sulfates, the sulfates would
not be transposed to perchlorates by this treatment.

[10] 2 ml. of 9 M HClO$_4$ in 1 liter of absolute alcohol.

[11] The solubility of $KClO_4$ in 100 ml. of absolute alcohol containing 0.2%
HClO$_4$ is 0.0028 g. at 21°; while for 98.8% alcohol containing 0.2% HClO$_4$
the solubility in 100 ml. is 0.010 g. at 25°.   For further solubility data, see
G. P. Baxter and M. Kobuyashi, *J. Am. Chem. Soc.*, **39**, 249 (1917).

absolute alcohol containing 0.2% perchloric acid.   Wash the precipitate on the filter seven or eight times with 2 ml. portions of the same alcohol solution, dry for an hour or so at 125°–130° and weigh as $KClO_4$.   From this weight calculate the amount of K_2O.

473. *Determination of Sodium.* — The sodium is determined by difference as follows: From the results for potassium, calculate the weight of potassium chloride; subtract this weight from that of the combined chlorides; the difference will be the weight of sodium chloride.   From the weight of sodium chloride so found, calculate the weight of Na_2O.   Sodium can be determined directly by precipitating it as $(UO_2)_3ZnNa(CH_3CO_2)_9 \cdot 6H_2O$.[12]

474. Examples.

1. In the analysis of a silicate rock the following results were obtained:

Wt. of Sample for SiO_2 "Combined Oxides,"	
Fe_2O_3, CaO and MgO	1.0048 g.
Crucible	35.3218 g.
Major portion of SiO_2	
Crucible + Impure SiO_2 before adding HF	35.8921 g.
Crucible + contents after adding HF	35.3220 g.
"Combined Oxides"	
Crucibles + "Combined Oxides"	35.5664 g.
SiO_2 from "Combined Oxides"	
Crucible + SiO_2 before adding HF	35.3269 g.
Crucible + contents after adding HF	35.3215 g.
Titration of Fe in "Combined Oxides"	
ml. 0.01326 M $KMnO_4$	16.15 ml.
Calcium	
Crucible	35.3212 g.
Crucible + CaO	35.3503 g.
Magnesium	
Crucible	35.3211 g.
Crucible + $Mg_2P_2O_7$	35.3761 g.
Separate Sample for K and Na	0.5126 g.
"Combined Chlorides"	
Evaporating dish + "Combined Chlorides" + SiO_2 impurity	18.1443 g.
Evaporating dish + SiO_2 impurity	18.1203 g.
Potassium	
Evaporating dish + Platinum	22.3174 g.
Evaporating dish	22.2954 g.

Calculate the per cent of each of the following: SiO_2, "Combined Oxides," Fe_2O_3, Al_2O_3, CaO, MgO, "Combined Chlorides," K_2O and Na_2O.

[12] Barber and Kolthoff, *J. Am. Chem. Soc.*, **50**, 1625 (1928).

CHAPTER XXIV

ELECTROMETRIC METHODS

475. General Considerations. — Electrometric methods find application in determinations of ion concentrations and in titrations, particularly when the color or composition of the solution under investigation is such as to interfere with the use of an indicator. Electrometric methods can be divided into (1) *Potentiometric Methods*, in which the measurement of a potential can be used to determine the concentration of an ion, or the measurement of the rate of change of potential can be used to locate the end point of a titration; and (2) *Conductimetric Methods*, in which the change in conductance of a solution during titration is used to locate the end point.

We will now consider potentiometric methods of determining ion concentrations and by way of illustration we will select the determination of pH.

476. Potentiometric Methods of Determining pH. — There are a great many instances in scientific investigation or in the industrial applications of science which demand accurate determinations of pH of solutions. We will now consider some of the ways in which this can be accomplished.

477. *The Determination of pH by Comparison of a Hydrogen Indicator Electrode with a Normal Hydrogen Reference Electrode.* — When a hydrogen electrode is used as a reference electrode in pH determinations, it is advisable to have the electrode vessel so constructed that oxygen can be excluded. Electrode vessels of the types shown in Figure 88 are satisfactory for this purpose.

If we place a hydrogen electrode in the solution under investigation in *B* of Figure 89 to serve as an indicator electrode and connect it to a normal hydrogen reference electrode in *A* and a potentiometer *P*, and then saturate both solutions with

hydrogen at one atmosphere of pressure, the difference of potential, E, between the two electrodes may be used to calculate the pH
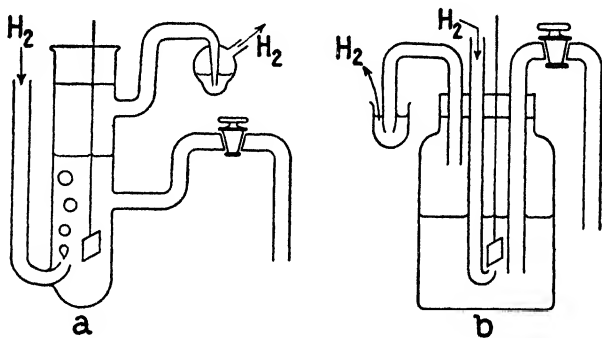
Fig. 88

Types of Hydrogen Electrode Vessels

and the hydrogen ion concentration of the solution in B.   The potential e_H^o of the normal hydrogen electrode has been arbitrarily taken as zero in the scale of potentials and, as we have seen in
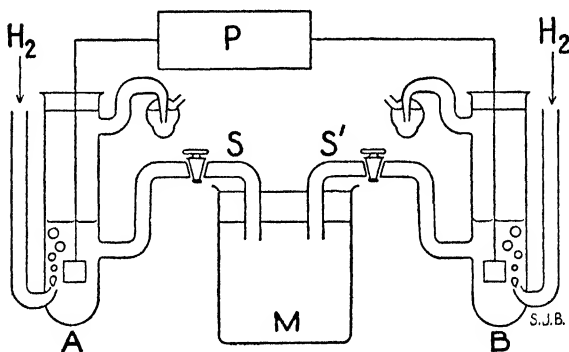
Fig. 89

Assembly Using a Normal Hydrogen Reference Electrode and a Hydrogen Indicator Electrode for the Determination of pH

§ 308, the potential e_H of the hydrogen ion-hydrogen system in B is given approximately by

$$e_H = 0.0001983 \; T \log [H^+].$$

Employing the activity of hydrogen ion a_{H+} instead of concentration we have the more correct expression,

$$e_H = 0.0001983 \ T \log a_{H+}.$$

Since

$$pH = -\log a_{H+},$$

it follows that

$$e_H = -0.0001983 \ T \ pH.$$

The measured difference of potential, E, between the two electrodes can be expressed as follows

$$E = e_H^o - e_H = 0 - (-0.0001983 \ T \ pH)$$

or

$$E = 0.0001983 \ T \ pH$$

whence,

$$pH = \frac{E}{0.0001983 \ T}.$$

By way of illustration, let us suppose that in measuring the voltage of the cell,

$$(Pt) H_2 (1 \text{ atmos.}) (\text{unknown solution}) \| H^+ (1.2M) H_2 (1 \text{ atmos.}) (Pt)$$
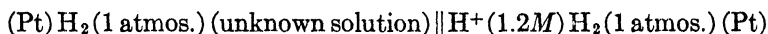
the normal hydrogen electrode was found to be more positive than the electrode in B by 0.1773 volts at 25°. This relationship is shown diagrammatically in Figure 90. The pH of the solution in B is then obtained from

$$pH = \frac{0.1773}{0.0001983 \ (273 + 25)} = 3.0.$$
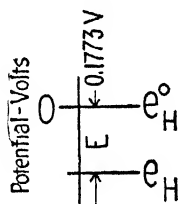
Fig. 90
Relationship between the Potential of a Normal Hydrogen Electrode and a Hydrogen Electrode in Solution Having a pH of 3.0

In order to illustrate the calculation of the hydrogen ion concentration let us assume that the solution is HCl. The activity of the H^+ is 1×10^{-3}. Referring to the table of activity coefficients of HCl (Table 68) we note that a $0.001 \ M$ HCl solution has an activity coefficient, f, of 0.965, hence an activity of 0.001×0.965, or 0.000965. For the slightly higher concentration corresponding to an activity of 1×10^{-3}, the activity coefficient is still practically

the same, hence the concentration of hydrogen ion will be

$$\frac{0.001}{0.965} = 0.00104 \ M.$$

When the potential of e_H° is negative with respect to e_H, the measured difference of potential, E, is considered negative. Under these conditions the hydrogen ion activity being determined is greater than one and the pH value is negative.

Table 68 [1]

ACTIVITIES AND ACTIVITY COEFFICIENTS OF HCl
AT VARIOUS CONCENTRATIONS

Concentration	Activity	Activity Coefficients
0.001	0.000965	0.965
0.005	0.00464	0.928
0.010	0.00904	0.904
0.050	0.04145	0.829
0.100	0.0796	0.796
0.500	0.379	0.757
1.000	0.810	0.810
2.000	2.038	1.019
3.000	3.960	1.320
4.000	7.048	1.762

The hydrogen electrode has some marked disadvantages, among which are the necessity of covering the surface of the electrode with platinum black to serve as a catalyst for the reaction

$$2 \ e + 2 \ H^+ \rightleftarrows H_2,$$

the danger of poisoning the catalyst, the length of time required to establish equilibrium, the necessity of supplying pure hydrogen at a known pressure and the necessity of excluding oxygen. Also, the use of the hydrogen electrode is unsatisfactory in solutions of very small conductance, in solutions containing strong oxidant-reductant systems, and in solutions from which gases are being evolved.

[1] For more extensive tables covering other electrolytes consult H. S. Taylor, "A Treatise on Physical Chemistry," Vol. I, 2nd ed., pp. 769 and 772, D. Van Nostrand Co., Inc., New York, 1930.

Some of these difficulties are avoided by using the saturated calomel electrode as a reference electrode in place of the normal hydrogen electrode.

478. *The Determination of pH by Comparison of the Hydrogen Indicator Electrode with a Saturated Calomel Reference Electrode.* — The calomel reference electrode finds wide use due to its simplicity as explained in § 305; the system involved in this electrode is

$$2 \, e + Hg_2^{++} \rightleftarrows 2 \, Hg.$$
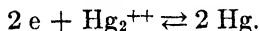
The mercury used must be of high purity and the mer-

Fig. 91

Saturated Calomel Electrode

curous ion must be supplied by means of a saturated solution of especially pure mercurous chloride. In the *saturated calomel electrode*, this solution is also saturated with respect to potassium chloride (about $3.5 \, M$). When the solution is normal with respect to potassium chloride, the electrode is referred to as the *normal calomel electrode* and when it is tenth normal with respect to potassium chloride, it is known as the *tenth normal calomel electrode*. Figure 91 shows the important features of a saturated calomel electrode, containing the pure mercury, M, solid Hg_2Cl_2 and solid KCl, C, and the solution D, saturated with both Hg_2Cl_2 and KCl.
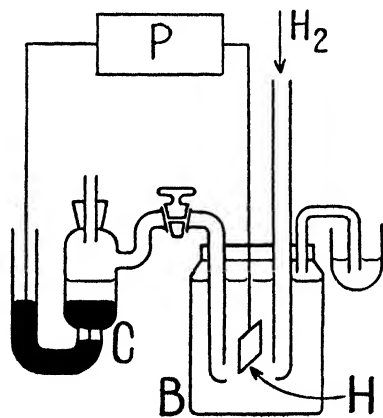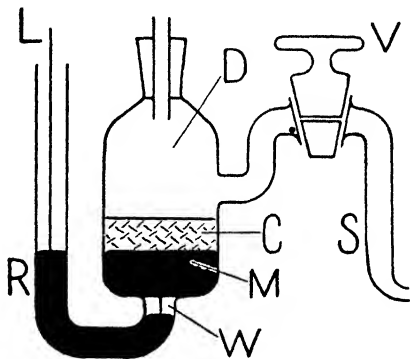
Fig. 92

Assembly Employing Calomel Reference Electrode and Hydrogen Indicator Electrode for Determination of pH

S is a salt bridge and R is a tube containing mercury used to make contact with the wire L. The platinum wire W serves to connect the pure mercury, M, with the mercury in R.

In order to determine the pH of a solution, we can use the apparatus shown in Figure 92. Let us suppose that the solution under examination is placed in B and that C is a saturated calomel electrode, P a potentiometer, and H a hydrogen electrode. When the solution in B becomes saturated with hydrogen at 25°, the potential e_H of the hydrogen electrode, as we have seen in § 477, may be expressed by

$$e_H = 0.0001983 \ T \log a_{H^+}$$

or

$$e_H = -0.0001983 \ T \ \text{pH}.$$

The potential of the calomel electrode, e_C, has a value of $+0.2458$ volts at 25°. Let us represent the measured difference of potential between the calomel electrode and the electrode in B by E. Then at 25°

$$E = e_C - e_H = 0.2458 - (-0.0001983 \ T \ \text{pH})$$

At some other temperature t

$$E = e_C - e_H + 0.00076 \ (25 - t)$$
$$= 0.2458 - (-0.0001983 \ T \ \text{pH}) + 0.00076 \ (25 - t)$$

where $0.00076 \ (25 - t)$ is the change in potential of the combination for the change in temperature $25 - t$. Whence

$$\text{pH} = \frac{E - 0.2458 - 0.00076 \ (25 - t)}{0.0001983 \ T}$$
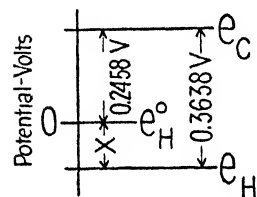
Fig. 93

Relationship between Potential of a Saturated Calomel Electrode and a Hydrogen Electrode in a Solution Having a pH of 2.0

Let us suppose, by way of illustration, that, on measuring the difference of potential, at 25°, between the calomel electrode and the hydrogen electrode of the cell
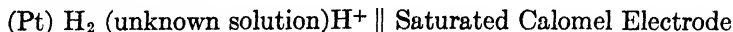
(Pt) H_2 (unknown solution)$H^+ \parallel$ Saturated Calomel Electrode

the hydrogen electrode was found to be negative with respect to the calomel electrode to the extent of 0.3638 volts. The value of E is then $+0.3638$ volts. This relationship is shown in Figure 93, in which X is the difference of potential which measures the

pH of the unknown solution. The pH of the solution in B is then obtained as follows:

$$\text{pH} = \frac{0.3638 - 0.2458 - 0.00076\,(25 - 25)}{0.0001983\,(273 + 25)} = 2.0$$
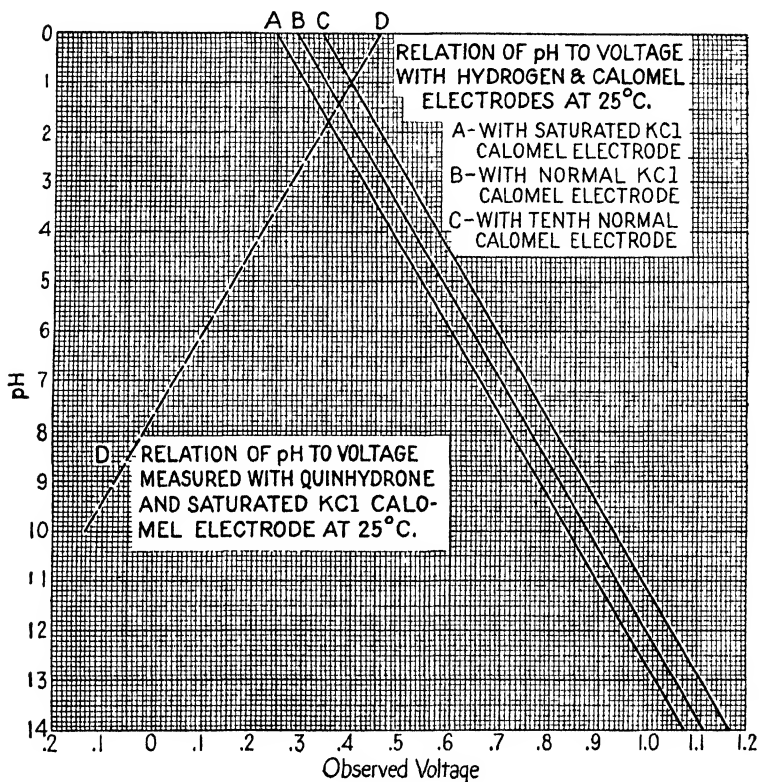
Fig. 94

Relationship between pH and Observed Voltage when Using Hydrogen Electrode and Saturated, Normal and Tenth Normal Calomel Electrodes; also when Using Quinhydrone and Saturated Calomel Electrodes

If, in measuring E, the calomel electrode is found to be negative with respect to the hydrogen electrode, then the value of E must be considered to be negative. If E has a negative value, or if the hydrogen electrode is negative with respect to the calomel

electrode by less than the potential of the calomel electrode, namely 0.2458 volts at 25°, the hydrogen ion activity is greater than one and the pH value will be negative.

The relationship between the pH of a solution and the observed voltage at 25° when a hydrogen indicator electrode and a saturated, a normal, or a tenth normal calomel reference electrode is used, is given approximately by curves *A*, *B* and *C* respectively of Figure 94.

479. Determination of pH by Comparison of the Quinhydrone Indicator Electrode with the Calomel Reference Electrode. — To avoid the inconvenience encountered in using a hydrogen electrode in the solution being tested, it is often advantageous to use a quinhydrone electrode as an indicator electrode. Quinhydrone, $C_6H_4O_2 \cdot C_6H_4(OH)_2$, when dissolved in solution yields the following equilibrium,

$$C_6H_4O_2 \cdot C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + C_6H_4(OH)_2$$
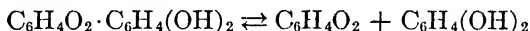
in which an equal number of molecules of quinone and hydroquinone are formed from the quinhydrone. The quinone and hydroquinone act as oxidant and reductant respectively of the system,

$$2\,e + 2\,H^+ + C_6H_4O_2 \rightleftarrows C_6H_4(OH)_2$$
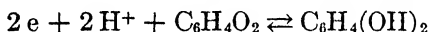
the potential of which may be expressed as follows,

$$e_Q = e_Q^\circ + \frac{0.0001983\ T}{2} \log \frac{a_{C_6H_4O_2} \times a_{H^+}^2}{a_{C_6H_4(OH)_2}}.$$

Since, under the conditions of use of this electrode, the activities of quinone and hydroquinone are equal, their activities cancel from the second term on the right and we have

$$e_Q = e_Q^\circ + \frac{0.0001983\ T}{2} \log a_{H^+},$$

whence, $\qquad e_Q = e_Q^\circ + 0.0001983\ T \log a_{H^+}$

and $\qquad e_Q = e_Q^\circ - 0.0001983\ T\ \mathrm{pH}.$

We see that the potential e_Q can be used as a measure of the hydrogen ion activity. The value of e_Q° is affected by changes in temperature and may be obtained from

$$e_Q^\circ = 0.6990 + 0.00074\ (25 - t).$$

In determinations of pH by means of the quinhydrone electrode, it is not necessary that the electrode be covered with platinum black. A bright platinum or gold wire or foil is satisfactory. Figure 95 shows the apparatus which may be used in pH deter-

minations. The beaker B contains the solution under investigation to which the quinhydrone is added and in which the electrode Q is inserted. This electrode is connected to the potentiometer P which in turn is connected to the calomel reference electrode C. By this arrangement the potential of Q can be compared directly with C. Since the potential of C has previously been compared with the zero potential of the normal hydrogen electrode, we can now obtain the potential of Q with respect to this zero potential.
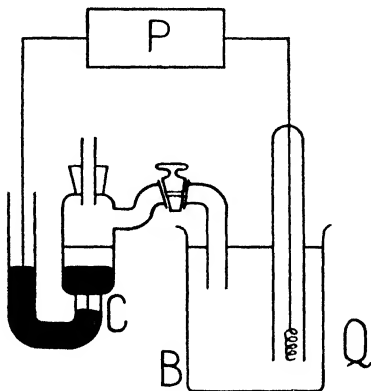
Fig. 95

Assembly Employing Calomel Reference Electrode and Quinhydrone Electrode for Determination of pH

Letting E represent the measured difference of potential between the calomel and quinhydrone electrodes, we have

$$E = e_Q - e_C$$

and

$$E = (0.6990 - 0.0001983\ T\ \text{pH}) - 0.2458 - 0.00002\ (25 - t)$$

where $0.00002\ (25 - t)$ is the change in potential of the combination for the temperature change $25 - t$. Then

$$\text{pH} = \frac{0.4532 - 0.00002\ (25 - t) - E}{0.0001983\ T}$$

By way of illustration, let us suppose that on measuring the difference in potential between the quinhydrone electrode and the calomel electrode at 25°, the former was found to be positive with respect to the calomel electrode to the extent of 0.2320 volts. This relationship is shown in Figure 96, in which X is the difference

of potential which measures the pH of the unknown solution. The pH of the solution under investigation is then obtained as follows:

$$pH = \frac{0.4532 - 0.00002\,(25 - 25) - (+0.2320)}{0.0001983\,(273 + 25)} = 3.74$$

If, in measuring E at 25°, the quinhydrone electrode is found to be positive with respect to the calomel electrode by more than 0.4532 volts, the pH value will be negative. When the quinhydrone electrode is negative with respect to the calomel electrode, the value of E is considered to be negative.

The relationship between the pH of a solution and the observed voltage at 25° when a quinhydrone indicator electrode and a saturated calomel reference electrode are used is given approximately by curve D of Figure 94.

The quinhydrone electrode has some important limitations. One of these is due to the fact that hydroquinone can undergo the following reaction

$$C_6H_4(OH)_2 + 2\,OH^- \rightleftharpoons C_6H_4O_2^- + 2\,H_2O.$$

Fig. 96

Potential Relationships in the Determination of pH by Means of Saturated Calomel Reference Electrode and Quinhydrone Indicator Electrode
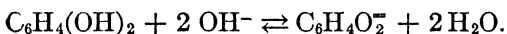
When this reaction takes place to an appreciable extent, sufficient hydroquinone is converted into hydroquinone ion so that the concentrations of quinone and hydroquinone are no longer substantially equal, hence their activities are not eliminated from the potential equation and the potential is no longer a measure of the hydrogen ion activity of the solution.[2] This limits the use of the quinhydrone electrode to well buffered solutions having a pH less than 8 and to unbuffered solutions having a pH less than 4. The potential of the quinhydrone electrode is also affected by the presence of oxidant-reductant systems which may

[2] LaMer and Parsons, *J. Biol. Chem.*, **57**, 613 (1923).

bring about oxidation of the hydroquinone or reduction of the quinone. The presence of high concentrations of salts also affects the potential to some extent.[3]

480. Determination of pH by Comparison of the Glass Electrode with the Calomel Reference Electrode. — The glass electrode has the marked advantage over the quinhydrone or hydrogen electrodes of not being affected by the presence of oxidant-reductant systems. It is precise in unbuffered solutions, reaches equilibrium instantly, and does not require the adding of quinhydrone or hydrogen to the solution under examination. Since it can be made of very small size, it can be used in the study of very small samples.

Figure 97 shows some of the important features of a glass electrode and the circuit in which it is used. The glass tube T, which is closed at its lower end by means of a very thin film of glass G, contains hydrochloric acid. A silver-silver chloride electrode or a quinhydrone electrode Q, immersed in the
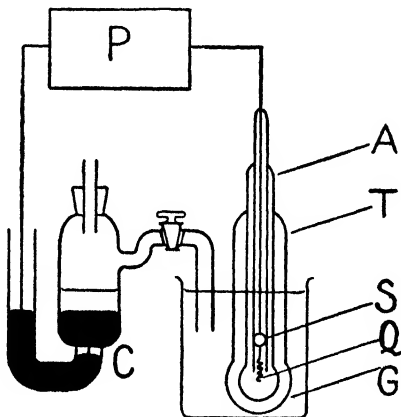
Fig. 97

Assembly Employing Calomel Reference Electrode and Glass Electrode for Determination of pH

hydrochloric acid, is connected to the potentiometer P. When a silver-silver chloride internal electrode is used, the tube A may be omitted. When a quinhydrone electrode is used, the electrolyte in A makes contact with that in G through the small hole S. A calomel reference electrode C is connected to the potentiometer. From the difference of potential E between the electrode Q and the calomel electrode C, as measured by the potentiometer P, the pH of the solution in B can be determined. When the tube T is inserted in the solution under investigation, a potential is produced at the interfaces of the glass film G and the two solutions with

[3] Hovorka and Dearing, *J. Am. Chem. Soc.*, **57**, 446 (1935).

which it is in contact.   This potential appears to be produced by the passage of some hydrogen ions through the glass film from the solution containing the higher hydrogen ion concentration to that in which the hydrogen ion concentration is less.   The potential of the glass electrode can be represented by

$$e_G = e_G^o + 0.0001983 \; T \log a_{H^+}.$$

The value of e_G^o depends in part on the potential of the internal electrode Q and in part on the characteristics of the glass film G

Fig. 98

Potential Relationships in Determining e^o for a Glass Electrode

and can be determined by measuring the difference of potential between the glass electrode and a hydrogen electrode in the same solution. This difference of potential may be expressed by,

$$e_G - e_H = e_G^o + 0.0001983 \; T \log a_{H^+}$$
$$- 0.0001983 \; T \log a_{H^+} = e_G^o.$$

Instead of determining e_G^o by comparing it directly with a hydrogen electrode, it is preferable to compare it with a saturated calomel electrode in a solution of known pH and calculate the difference of potential between the glass electrode and the hydrogen electrode.   This difference is e_G^o.   Representing the observed difference of potential between the glass electrode and the calomel electrode by E', we have at 25°

$$e_G^o = e_G' - e_H = E' + 0.2458 - 0.0001983 \; T \log a_{H^+}. \qquad (1)$$

When the difference of potential between the glass electrode and calomel electrode is found to be 0.2701 volts at 25° in a solution having a pH of 3.00, we have

$$e_G^o = 0.2701 + 0.2458 + 0.1773 = 0.6932 \text{ volts.}$$

These relationships are shown diagrammatically in Figure 98. We can make use of the value of e_G^o, in a pH determination.   Thus if in the determination of pH, we let E represent the measured

difference of potential between the glass electrode and the calomel electrode, then

$$E = e_G - e_c$$

and

$$E = e_G^o + 0.0001983\ T \log a_H - 0.2458 + 0.00002\ (25 - t)$$

where $0.00002\ (25 - t)$ is the change in E for temperature change $25 - t$. Then

$$\mathrm{pH} = \frac{e_G^o - 0.2458 - 0.00002\ (25 - t) - E}{0.0001983\ T} \qquad (2)$$

Since e_G^o is affected by changes in temperature, the value of e_G^o used in calculating the pH should be that corresponding to the temperature at which E is determined. To illustrate the calculation of the pH of a solution, let us suppose that at 25°, e_G^o is 0.6932 volts and E is 0.2260 volts, then

$$\mathrm{pH} = \frac{0.6932 - 0.2458 - 0.2260}{0.0001983\ (273 + 25)} = 3.75.$$

These relationships are shown diagrammatically in Figure 99, in which X is the difference of potential which measures the pH of the unknown solution.

In practical work in pH determination it is not necessary to know the actual value of e_G^o and the actual value of the reference electrode, since these values are the same in the solution of known pH and in the unknown solution. All that is required is E', the difference of potential between the reference electrode and the glass electrode in a solution of known pH, and E, the difference of potential between the reference electrode and the glass electrode in the unknown solution. We have then

Fig. 99

Potential Relationships in Determining pH of Solution by Means of Saturated Calomel Electrode and Glass Electrode

$$\mathrm{pH}_{\text{unknown}} = \mathrm{pH}_{\text{known}} + \frac{E' - E}{0.0001983\ T}.$$

Thus for the above illustration in which E' was 0.2701 volts, E was 0.2260 volts, the known solution had a pH of 3.0, and the

temperature was 25° for the determination of both E' and E we have

$$\text{pH}_{\text{unknown}} = 3.0 + \frac{0.2701 - 0.2260}{0.0591} = 3.75.$$

There are limitations to the use of the glass electrode. When the glass film is sufficiently thin so that its electrical resistance is not excessive, it is often quite fragile. Although between a pH of 1 and 8.5, the potential of a glass electrode may be obtained from

$$e_G = e_G^\circ - 0.0001983 \, T \, \text{pH},$$

when the pH is above 8.5, e_G acquires a value more positive than that corresponding to the pH in the above equation. This error appears to be due to the positive ions in solution other than the hydrogen ion and is particularly pronounced when these ions are univalent.[4] In solutions more acid than a pH of 1, e_G has a value more negative than that corresponding to the pH in the above equation.[5]

481. The Principle of the Poggendorf Type of Potentiometer. — If a voltmeter were to be used in measuring the difference of potential between the electrodes of a cell, a current would have to flow from the cell to operate the voltmeter. This current would set up a back electromotive force within the cell which would change the voltage of the cell. Thus we see that the reading of the voltmeter would not give the original difference of potential which we set out to measure. It is important, therefore, that the voltage be measured while no current is flowing in the cell circuit (null method). This can be accomplished by means of a potentiometer.

In the circuit shown in Figure 100, AB is a resistance wire of uniform resistance throughout its entire length and stretched along the graduated scale M. The cell W is known as the working cell, R is a variable resistance, G a galvanometer, K a key, S a switch, C a standard cell of known difference of potential and E the cell of unknown difference of potential.

[4] M. Dole, "Principles of Experimental and Theoretical Electrochemistry," p. 433 of reference given in § 11.

[5] MacInnes and Belcher, *J. Am. Chem. Soc.* **53**, 3315 (1931); M. Dole, *J. Am. Chem. Soc.* **54**, 3095 (1932).

Before an unknown voltage can be determined, the potentiometer must be standardized against the standard cell C. Let us suppose that the standard cell has a value of 1.0185 volts. The adjustable contact L is placed 1,018.5 units along the scale from A. The current from W is then adjusted by means of the variable resistance R until the difference in potential between A and L is equal and opposite to the voltage of the standard cell, namely 1.0185 volts. Under these conditions, no current will
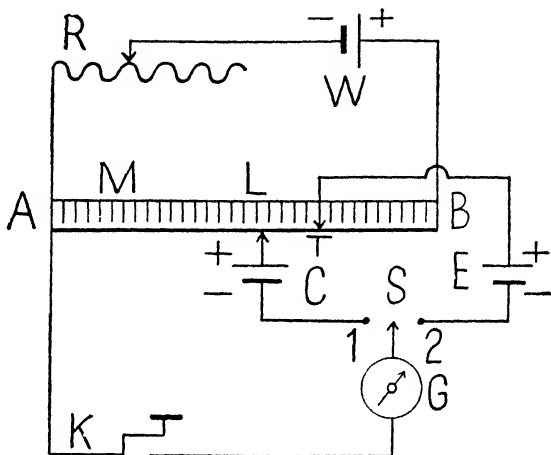
Fig. 100

Circuit of Poggendorf Type of Potentiometer

flow through the galvanometer when the switch S is turned so as to make contact with 1 and key K is closed, provided the internal resistance of C is greater than that of W. When, however, the internal resistance of C is less than that of W, the standard cell C will furnish the current through AB and no current will flow through the circuit containing W and R. This can generally be avoided by providing a working cell of very low internal resistance. Since the difference in potential of 1.0185 volts has been established across 1,018.5 units of the uniform resistance AL, it follows that one unit corresponds to 0.001 volts.

We can now proceed to the determination of the voltage of E. Without changing the variable resistance R, the switch S is

turned so as to make contact with 2 and the sliding contact T is adjusted until a point is reached at which no current flows through the galvanometer G when the key K is closed. The difference of potential between A and T is then equal and opposite to that of the cell E. Let us suppose that when this condition exists, T is 1,203.2 units from A. The voltage of E is then 1,203.2 × 0.001, or 1.2032 volts. If one of the electrodes of E is a reference electrode S of known potential, and the other is an indicator electrode I of unknown potential, we can calculate the potential of I from

$$E = e_I - e_s.$$

482. The Vacuum Tube Potentiometer. — It is often desirable in measuring the potential of a cell to use a potentiometer which will at no time permit a current to flow from the cell. A potentiometer of the Poggendorf type when properly adjusted can be made to operate without drawing a current from the cell; however, during the process of adjusting, current will flow. Recently potentiometers employing one or more vacuum tubes have been developed. An instrument of this type has the distinct advantage over the potentiometer of the Poggendorf type of not permitting an appreciable current to flow from the cell at any time. It is beyond the scope of this text to consider instruments of this sort in detail and a brief discussion of the principle of this type of instrument will suffice for our present purpose.[6]

G, P and F of Figure 102 are the grid, plate and filament respectively of the vacuum tube V. Figure 101 [7] shows some of the characteristics of a tube of this type. Curves A, B, and C show the relationship between the current flowing between the filament and the plate of a vacuum tube and the potential of the grid when the positive plate voltages are 10, 20 and 30 volts respectively. Curve D shows the relationship between the potential of the grid and the current flowing between the filament and the grid. We see from Figure 101 that the greater the positive

[6] For greater detail with respect to instruments employing vacuum tubes, see Kolthoff and Furman, "Potentiometric Titrations," reference given in § 11; also F. Muller, *Z. Electrochem.*, **36**, 923 (1930); and Treadwell, *Helv. Chem. Acta.*, **8**, 89 (1925).

[7] Adapted from J. H Morecroft, "Radio Phone Receiving," Chapter IV, D. Van Nostrand Company, New York, 1922.

potential on the plate, the greàter the plate current.   We also see
that with limited variation in grid voltage and a properly adjusted
plate voltage, we can obtain approximately a linear variation
of plate current with grid voltage.   Curve D shows that when
the grid is at free grid potential the grid current is zero.   By
free grid potential is meant the potential of the grid when dis-
connected from the rest of the circuit.   When the grid is more
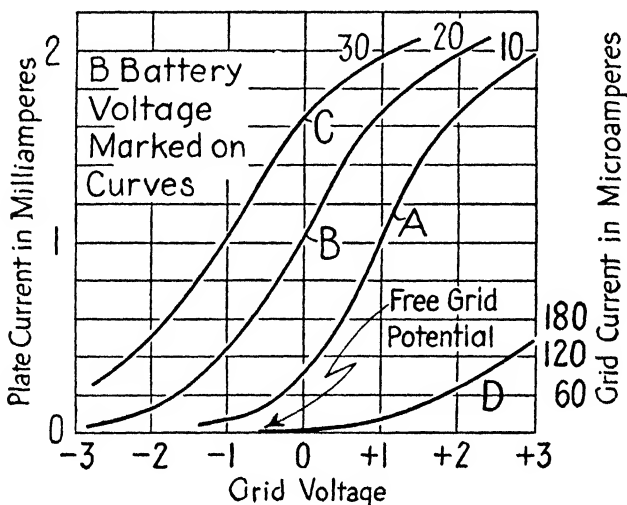
Fig. 101
Vacuum Tube Characteristics

negative than the free grid potential the grid current is still
practically zero.   The tube should be operated with its grid at
potentials more negative than the free grid potential.

   In Figure 102, V is the vacuum tube containing the filament F,
the plate P and the grid G.   The battery A supplies current to
F, thereby heating it sufficiently to cause it to emit electrons.
The resistance R is used to regulate the current through F.   The
battery B is connected to P by means of its positive terminal,
thereby making it possible for P to attract electrons from F.
The battery C is connected to G by means of its negative terminal,

thereby preventing electrons from passing from F to G. The resistance R_2 is used to regulate the negative potential of the grid. The voltmeter M, connected across the resistance R_3, measures the IR drop in R_3 and thus the current between the filament and the plate. The cell furnishing the unknown potential, E, consists of the reference electrode S and the indicator electrode I.

To operate this circuit, before connecting the cell E, the grid is disconnected from the rest of the circuit. The grid is now at free grid potential. The plate current is then measured by means of M. The grid is now connected as shown and with the cell E still disconnected R_2 is adjusted until the plate current has the same value as it had when the grid was disconnected. The grid is now at free grid potential. Any potential now impressed on the grid which makes the grid more negative will lower the plate current, and the value of the plate current can be used as a measure of the potential of the grid. Hence, when the cell E is connected in such a way as to make the grid more negative than the free grid potential, the plate current will be reduced proportionally. At the same time no appreciable current will pass through the cell. In potentiometric titrations a strict proportionality between plate current and cell voltage is not required since at the end point the cell voltage changes very rapidly, causing in turn such a rapid change in plate current that the end point can be easily detected.

For practical purposes the advantages of stability and sensitivity

Fig. 102

Vacuum Tube Potentiometer Circuit

can be obtained from somewhat modified circuits. The circuit
shown in Figure 103, designed by Garman and Droz,[8] which
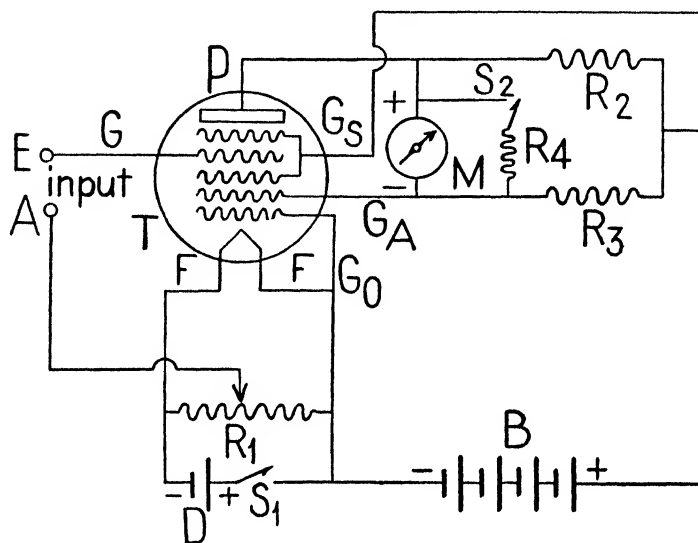
Fig. 103

Vacuum Tube Potentiometer Circuit, Possessing Stability and
Sensitivity

operates from batteries is to be recommended.   The specifications
for this circuit are as follows:

T Vacuum Tube, Sylvania 1A7G

R_1 Potentiometer, 5,000 Ω

R_2 Resistance, 1,000 Ω

R_3 Resistance, 1,500 Ω

R_4 Resistance, 600 Ω

B Battery, 45 volts

D Dry cell, 1.5 volts

M Meter, Weston Type 301 (0–200 microamperes) I.R. 660 Ω

S_1 Toggle switch

S_2 Toggle switch

[8] Garman and Droz, Private Communication, 1938.   For further details
regarding this circuit the reader is referred to R. L. Garman and M. E. Droz,
Washington Square College, New York University, New York.

In the use of this circuit the following operations should be performed in the order listed,

1. Close S_1 and S_2
2. Short A and E
3. Adjust R_1 until the meter reads zero
4. Remove the connection between A and E
5. Connect the electrodes of the cell to be measured to A and E in such a manner that the electrode connected to E is the one, the potential of which becomes more negative with the progress of the titration reaction
6. Open S_2 and readjust the potentiometer until the meter reads zero
7. Titrate

When a glass electrode is used as the indicator electrode, lead E should be a shielded wire of as short a length as possible; lead A and the shield of lead E should be grounded.

For special equipment used in connection with potentiometric and conductimetric determinations the reader is referred to the Leeds and Northrup catalogues cited in § 11.

483. Exercise No. 56. Determination of the pH of a Solution by Means of a Quinhydrone Indicator Electrode and Calomel Reference Electrode. — Prepare a saturated calomel electrode according to the foregoing directions and construct the electrical circuit shown in Figure 95, making use of a potentiometer of the Poggendorf type described in § 481. Before determining the pH of the unknown solution, test the equipment on a solution of known pH furnished by the instructor. If satisfactory results are obtained, measure the pH of an unknown solution furnished by the instructor.

484. Exercise No. 57. Determination of the pH of a Solution by Means of a Glass Electrode and Calomel Reference Electrode. — Construct the circuit shown in Figure 97, inserting a vacuum tube potentiometer of the type shown in Figure 103 in place of the galvanometer of a Poggendorf type of potentiometer. Adjust the resistance bridge until the meter reads zero. (The plate current is now the same as when the terminals of the vacuum tube circuit are short circuited.) Using a solution of known pH

determine the difference of potential E' between the indicator and reference electrodes. Observe the temperature of the solution. Proceed then to obtain the difference of potential E between the indicator and reference electrodes in the unknown solution. In measuring E' and E both solutions must be at the same temperature. Calculate the pH of the unknown solution.

485. Potentiometric Titrations. — When we carry out a titration of one substance with another, a change in potential of the solution being titrated takes place during the course of the titration. The rate of change of potential is not uniform, however, but passes through a maximum. This is illustrated in Figure 104 by the curve obtained when 25.00 ml. of 0.1 M hydrochloric acid, diluted to 125 ml., is titrated at 25°, with 0.1 M sodium hydroxide solution, using a hydrogen indicator electrode and a saturated calomel reference electrode. The steepest portion of
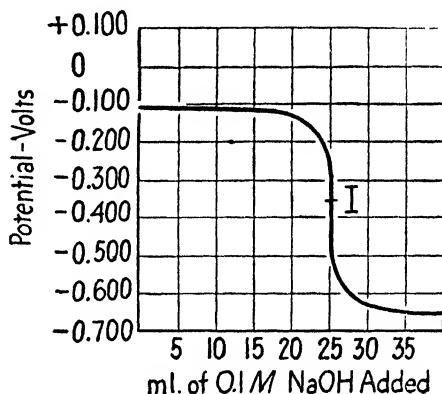
Fig. 104

Potential Change in Titration of Hydrochloric Acid with Sodium Hydroxide Solution

the curve is at I, which is known as the point of inflection and is the point of maximum rate of change of potential. When the point of inflection of a titration and the stoichiometric point are close together, then any method which will locate the point of inflection can be used to locate the stoichiometric point. The point of inflection can be located by means of an indicator which produces a change of appearance of the solution at some point on the upright portion of the curve and thus furnishes an end point close to the point of inflection and, hence, close to the stoichiometric point. Another method of locating the point of inflection is to insert an indicator electrode in the solution being titrated and, by means of a potentiometer circuit, to determine the point

of maximum rate of change of potential.   In titrations in which
the stoichiometric potential is known in advance, the potential
of the solution can be measured during the course of the titration
by means of an indicator electrode and the titration continued
until the stoichiometric potential has been reached.

In some titrations, the point of inflection and the stoichiometric
point coincide exactly, while in others these points do not coincide.
In most quantitative
methods, this difference is
very small and can usually
be neglected.   Another
source of error, however,
must be considered.   The
shorter the upright por-
tion of the curve and the
more gradual its slope,
the more difficult it will
be to find an indicator
which will produce an end
point close to the point
of inflection, and the
more difficult it will be to
determine, by means of an
indicator electrode, the
point of maximum rate
of change of potential.
Whenever possible, the
reacting substances and
the conditions involved
in a titration should be
such as to produce a curve with a long and nearly vertical upright
portion.   By plotting rate of change of potential against volume
of solution added, instead of plotting potential against volume,
we obtain a curve the maximum of which corresponds with the
point of inflection of the potential-volume curve.   Figure 105
shows the curve for the titration of Figure 104, when plotted
in this manner.

It will be convenient to classify potentiometric titrations with

Fig. 105

Rate of Change of Potential Plotted
Against Volume of Solution Added, in
Titration of Hydrocloric Acid with Sodium
Hydroxide Solution

respect to the type of reaction involved. We will consider ti-
trations involving (1) neutralization, (2) precipitation, and (3)
oxidation-reduction.

486. *Potentiometric Titrations Involving Neutralization.*—When
the acid and base involved are both strong electrolytes, the point
of inflection and the stoichiometric point will coincide and the
upright portion of the curve will be long and nearly vertical.
Figure 104 illustrates a titration of this type. It is relatively

easy with such titrations
to provide an end point
close to the stoichiometric
point. With respect to
neutralization reactions in
general, the more dilute
the solutions of acid and
base used, the shorter is
the upright portion of the
curve. When one of the
electrolytes involved is
weak and the other is
strong, the upright por-
tion of the curve in the re-
gion of the stoichiometric
point will be shorter and
have a more gradual slope
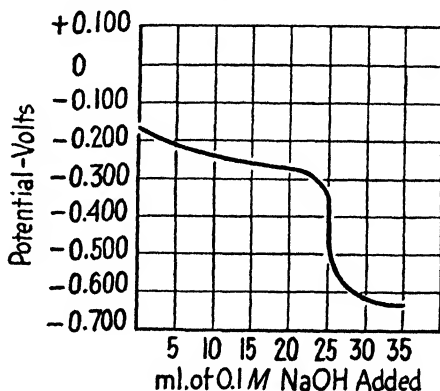
Fig. 106

Potential Change in Titration of Acetic
Acid with Sodium Hydroxide Solution

than when both electrolytes are strong, and consequently, a precise
location of the stoichiometric point will be more difficult. In titra-
tions of this type, although the point of inflection and the stoichio-
metric point do not exactly coincide, the difference between these
points is generally very small. As pointed out in § 138, this
difference varies inversely as the square root of the ionization
constant of the weak electrolyte, and inversely as the square root
of the stoichiometric concentration of salt at the stoichiometric
point. Figure 106 illustrates the curve for a titration of this
type, in which 25.00 ml. of 0.1 M acetic acid diluted to 125 ml.
was titrated at 25° with 0.1 M sodium hydroxide, using a satu-
rated calomel reference electrode. Figure 107 shows rate of
change of potential plotted against volume of base added for the

titrations illustrated in Figure 104 and Figure 106. It should be observed that the curve for the titration of hydrochloric acid yields a higher and more sharply defined maximum than that for acetic acid.
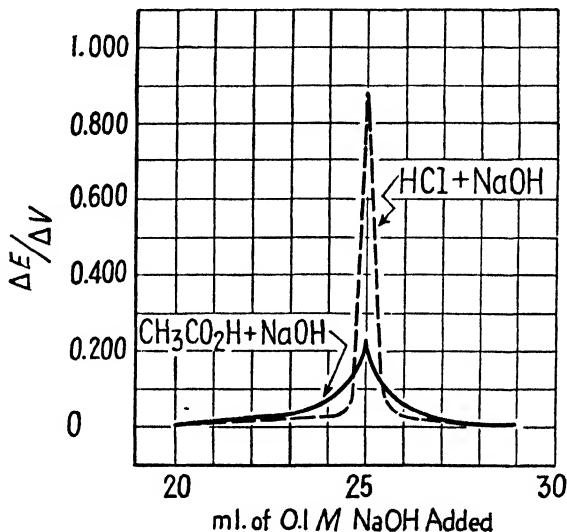
Fig. 107

Comparison of Maxima in Curves for Titrations of Hydrochloric and Acetic Acids with Sodium Hydroxide Solution

487. Exercise No. 58. Potentiometric Determination of Hydrochloric Acid in a Colored Solution by Titration with Sodium Hydroxide. — Construct the circuit shown in Figure 92, using a beaker in place of the bottle B. If a vacuum tube potentiometer of the type shown in Figure 103 is available, it may be used, in which case follow the directions given in § 482. If this type of potentiometer is used, lead E must be connected to the indicator electrode. Since the aim is not to determine accurately the pH of the solution but rather to locate the point of inflection of the titration curve, there is no need to purify the hydrogen used in the hydrogen electrode. The platinum foil in this electrode however must be freshly platinized. To accomplish this, clean it in hot $3M$ NaOH solution, rinse thoroughly with distilled water and

then use as the cathode for about five minutes in the electrolysis of a 0.06 M solution of K_2PtCl_6, employing a current density of about 0.015 amp./cm.² Rinse the platinized electrode with distilled water and keep under distilled water until required.

Measure carefully from a burette enough of the unknown solution to require about 25 ml. of standard 0.1M NaOH solution in the titration. Insert the calomel and hydrogen electrodes and saturate the solution with hydrogen. Titrate the solution, observing the volume of solution added and the value of E after each addition of NaOH solution. In the vicinity of the stoichiometric point add the NaOH solution, a drop at a time, taking care that the drops are all of the same size. Continue the titration until it is certain that the point of inflection has been passed. Plot the observed values of E against milliliters of solution added. Also plot $\Delta E_i/\Delta V$ against milliliters of solution added. Locate the end point and calculate the weight of HCl in the sample.

488. Potentiometric Titrations Involving Precipitation. — In precipitation titrations, the rate of change of potential as measured by a suitable indicator electrode passes through a maximum as shown by the curves of Figure 108 for the titration of chloride ion with silver ion. The length of the upright portion of the potential-volume curve or the height of the maximum for $\Delta E/\Delta V$

Fig. 108

Curves for Titration of Chloride Ion with Silver Ion

decreases with an increase in the solubility product of the precipitate formed. Thus AgI gives a higher maximum than AgCl

under similar conditions and AgCl gives a higher maximum at 5°
than it does at 25°. Since an increase in the total ion concen-
tration of a solution in contact with a precipitate increases the
solubility product, it has the effect of lowering the maximum
which can be obtained. As in the case of neutralization titrations,
the larger the volume of the solution at the stoichiometric point,
the lower the maximum. When the precipitate contains an
equal number of the two oppositely charged ions taking part in
the reaction, as in the reaction

$$Ag^+ + Cl^- \rightleftarrows AgCl,$$
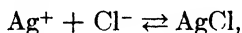
the point of inflection and the stoichiometric point will coincide
exactly. If, however, the reaction is of the type

$$2\ Ag^+ + C_2O_4^= \rightleftarrows Ag_2C_2O_4,$$

then, on titrating oxalate ion with silver ion, the point of inflection
will come after the stoichiometric point. In general, the point
of inflection will require the presence of an excess of the ion of
smaller valence. The magnitude of the difference between the
point of inflection and the stoichiometric point increases with an
increase in the volume of the solution at the stoichiometric point
and with an increase in the value of the solubility product.[9]

For the titration of chloride ion with silver ion, a silver indicator
electrode is used in conjunction with a reference electrode. By
means of the silver electrode the potential of the system

$$1\ e + Ag^+ \rightleftarrows Ag$$

can be determined. The value of this potential can be expressed
as follows,

$$e_{Ag^+,\ Ag} = e^{\circ}_{Ag^+,\ Ag} + 0.0001983\ T \log [Ag^+].$$

Since in a saturated solution of AgCl we have

$$[Ag^+]\ [Cl^-] = K_{AgCl},$$

it follows that in a saturated solution of AgCl, the potential of the
silver ion-silver system serves not only as a measure of $[Ag^+]$,
but of $[Cl^-]$ as well.

[9] For a more complete discussion of the subject of titrations involving
precipitation see "Potentiometric Titrations," by Kolthoff and Furman,
cited in § 11.

489. Exercise No. 59. Potentiometric Determination of Potassium Chloride in a Mixture of Potassium Chloride and Barium Nitrate. — Potassium chromate cannot be used as the indicator in titrating the unknown solution with silver nitrate solution, owing to the fact that the chromate ion would be removed from the solution as barium chromate.

Construct the circuit given in Figure 60 of Chapter XV, using a silver indicator electrode in beaker B and a saturated calomel reference electrode, R, in beaker S. Use either a Poggendorf type potentiometer or a vacuum tube potentiometer of the type shown in Figure 103. Use $0.05M$ NH_4NO_3 solution in beaker S and in the salt bridge.

Weigh out into 100 ml. beakers three portions of the sample, requiring about 25 ml. of standard $0.1M$ $AgNO_3$ solution in titration. Dissolve each sample in 50 ml. of distilled water. Prior to titration place the indicator electrode in the solution of the sample in beaker B and insert the salt bridge. During titration stir continuously and observe the value of the equilibrium potential E and the volume of solution added. In the vicinity of the stoichiometric point add the silver nitrate solution in a succession of equal sized drops, noting the value of E and the volume of solution added after each drop. Plot the curve for the titration and locate the end point. From the results of triplicate determinations and from the results of a moisture determination on separate portions of the sample, calculate the per cent of KCl in the sample on the moisture free basis.

490. *Potentiometric Titrations Involving Oxidation-Reduction.* — As explained in § 310, when an oxidation-reduction reaction is carried out by bringing together in the same solution two oxidant-reductant systems of different potentials, the equilibrium potential finally established will be intermediate between the potentials of the two systems involved. If the system of more negative potential is contained in a solution in a beaker and the solution containing the system of more positive potential is added from a burette, the potential of the solution in the beaker will undergo a change illustrated by the curve in Figure 109 for the titration of ferrous ion with ceric sulfate solution. The point of inflection of the curve generally occurs very close to the

stoichiometric point. When the number of electrons in the two systems involved is the same, the curve will be symmetrical with respect to the point of inflection. This is illustrated by Figure 109. In titrations of this type, the point of inflection and the stoichiometric point will exactly coincide. When, however, the two systems involve different numbers of electrons, the curve will not be symmetrical with respect to the point of inflection.

The curve in Figure 110 for the titration of titanous ion with stannic ion illustrates this type of titration. It should be observed that shortly before reaching the stoichiometric point, when there is an excess of titanous ions present, the change in potential for the addition of a given volume of solution is more abrupt than it is beyond the stoichiometric point with an excess of stannic ions present. Before the stoichiometric point is reached, the change in potential can be measured by the change in the ratio of

$$\frac{[Ti^{++++}]}{[Ti^{+++}]}.$$

A tenfold increase in this ratio will raise the potential 0.0591 volts at 25°, since only one electron is involved in the system. Beyond the stoichiometric point, the change in potential can be measured by the change in the ratio of

$$\frac{[Sn^{++++}]}{[Sn^{++}]}.$$

A tenfold increase in this ratio will raise the potential only 0.0295 volts at 25°, since there are two electrons involved in the system.

Fig. 109

Curve for Titration of Ferrous Ion with Ceric Sulfate Solution

The stoichiometric point in this titration will be reached after the point of inflection. In general, when interfering factors such as formation of a precipitate or a complex ion are absent, the point of inflection will occur on that side of the stoichiometric point having an excess of the system involving the smaller number of electrons.

The more incomplete the reaction at the stoichiometric point, the less the slope of the upright portion of the curve. When the stoichiometric point of a titration does not coincide exactly with the point of inflection of the curve, then the less the slope of the curve, the greater will be the differ-ence between these points. Also, the less the slope of the curve near the stoichiometric point, the greater the diffi-culty in locating the stoichiometric point by means of an indicator or an indicator elec-trode. When titanous

Fig. 110

Curve for Titration of Titanous Ion with Stannic Ion

ion is titrated with stannic ion, the reaction is relatively incomplete at the stoichiometric point, about 87 parts per thousand of tita-nous ion remaining unoxidized. In the curve for this titration, S is the stoichiometric point and I is the point of inflection. It is seen that when the end point differs from the stoichiometric point by as little as 0.01 volts, an error of 1 ml. is produced. From a consideration of the curves of Figure 109 and Figure 110, we see that the more nearly complete the reaction at the stoichi-ometric point, the more easily it lends itself to precise analytical methods. In general, when no interfering factors, such as complex formation or precipitation, enter into a titration, the greater the difference between the molar potentials of the systems involved, the easier it will be to locate precisely the stoichiometric point.

A gold foil may be used as the indicator electrode in titrations involving oxidation-reduction. This type of electrode has been previously described in § 305 in connection with its use in measuring oxidation-reduction potentials.

491. Exercise No. 60. Determination of Iron in a Mixture of Ferrous and Cobalt Sulfates. — Construct the circuit shown in Figure 111, using a gold electrode in B, a saturated calomel reference electrode and a Poggendorf type or vacuum tube type of potentiometer.

Follow the procedure given in § 347 up to the point where the unknown solution is ready to be titrated. Insert the indicator and reference electrodes. Titrate, observing the values of E and the corresponding volumes of potassium permanganate solution added during the course of the titration. In the neighborhood of the stoichiometric point, add the permanganate solution in a series of equal sized drops. Determine the end point from the curve of the titration, and, on the basis of the end point and the results of a determination of moisture on a separate portion of the sample, calculate the per cent of iron in the sample on the dry basis. Perform this determination in triplicate.

Fig. 111

Assembly for Potentiometric Titration of Iron

492. Conductimetric Methods. — If at the stoichiometric point of a titration, there is a marked change in the rate at which the conductance of the solution changes, the observance of this change of rate may make possible the location of the stoichiometric point. A change in the rate at which the conductance changes at the stoichiometric point may be brought about by a sudden change in the number of ions in the solution or by the replacement of ions in the solution by other ions of appreciably different mobility.

In conductimetric methods of analysis it is not necessary to determine in absolute terms the conductance of the solution being titrated. All that is required is to locate the point in the titration

at which the rate of change of the resistance of the solution changes. If the volume of the solution being titrated is large compared ,with the volume of solution added, so that the volume of, the solution being titrated remains practically constant, all that is necessary is to determine the resistance at two points preceding the stoichiometric point and at two points following the stoichiometric point. If in plotting resistance against volume of solution added, a straight line is drawn through the first pair

Fig. 112

Curve for Conductimetric Titration of Hydrochloric Acid with Sodium Hydroxide Solution

of points and another straight line is drawn through the second pair of points, the intersection of these lines will lie close to the stoichiometric point.

In the titration of HCl with NaOH we have

in burette   in cell at the end point

$$\overbrace{Na^+ + OH^-} + \underbrace{H^+ + Cl^-}_{\text{in cell at beginning}} \quad \rightarrow \quad \overbrace{Na^+ + Cl^-} + H_2O$$

From the beginning of this titration to the stoichiometric point, Na^+ is made to replace the more mobile H^+ and, consequently,
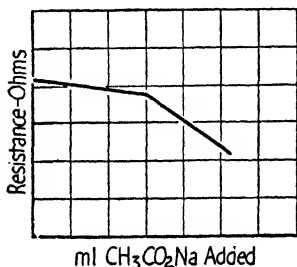
Fig. 113

Curve for Conductimetric Titration of Lead Nitrate with Sodium Acetate Solution

resistance of the solution rises. Just as soon as the stoichiometric point is passed, the concentration of the highly mobile OH^- is suddenly increased and, hence, the resistance drops. This titration yields a curve similar to that given in Figure 112.

In the titration, in neutral or alkaline solution of $Pb(NO_3)_2$ with CH_3CO_2Na, the weak electrolyte $Pb(CH_3CO_2)_2$ is formed and Na^+ replaces the less mobile Pb^{++}, with the result that the resistance falls

slowly. Beyond the stoichiometric point, a sudden increase in the concentration of the acetate ion causes the resistance to fall at an increased rate. The curve for this titration is similar to that shown in Figure 113.

In the titration of potassium chloride with silver nitrate we have

$$\overbrace{Ag^+ + NO_3^-}^{\text{in burette}} + \underbrace{K^+ + Cl^-}_{\text{in cell at beginning}} \rightarrow \overbrace{K^+ + NO_3^-}^{\text{in cell at end point}} + AgCl \downarrow$$
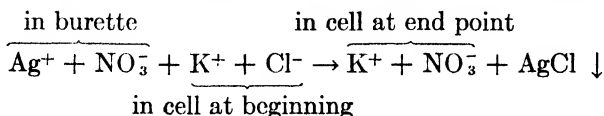
Until the stoichiometric point is reached, NO_3^- replaces the more mobile Cl^- in the solution with the result that the resistance rises slowly. Beyond the stoichiometric point, there is a sudden increase in the concentration of Ag^+ accompanied by a rapid decrease in resistance. The curve for this titration is similar to that shown in Figure 114.

Figure 115 shows the apparatus required to locate the stoichiometric point in a conductimetric titration. The solution to be titrated is contained in the conductance cell D, containing the two platinized platinum electrodes A and B. The cell is connected to an alternating current Wheatstone's bridge of the type designed by Jones and Josephs,[10] in which R_1 and R_2 are resistance arms of equal resistance, R_3 is a variable resistance, P is a pair of head phones, and C_1 is a variable capacitance with which to balance the capacitance of the conductance cell D. A pure, sine wave, high-frequency alternating current is supplied by an oscillator circuit connected to M and N. When A and B are in the solution in D, and S makes contact at 2, R_3 and C_1 are adjusted until the sound in the phones is at a minimum. We have then

Fig. 114

Curve for Conductimetric Titration of Potassium Chloride with Silver Nitrate Solution

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}.$$

[10] Jones and Josephs, *J. Am. Chem. Soc.*, **50**, 1049 (1928).

Before making the final adjustments of R_3 and C_1, S should be turned to make contact with 1 and R_5, R_6 and C_2 should be adjusted to a point of minimum sound in the phones in order to bring the bridge to the potential of the ground and thereby eliminate errors resulting from capacitance between the phones and the analyst. When making the final adjustments of R_3 and C_1, switch S should make contact with 2. For more detailed discussions of conductance measurements the reader is referred to "Experimental and Theoretical Electrochemistry" by Dole [11] and "Outlines of Theoretical Chemistry" by Getman and Daniels.[12]

493. Exercise No. 61. Conductimetric Determination of Potassium Chloride in a Mixture of Potassium Chloride and Barium Nitrate. — Dissolve in 300 ml. of distilled water an amount of sample requiring about 25 ml. of 0.1 M $AgNO_3$ solution. Making use of equipment similar to that described

Fig. 115

Assembly for Conductimetric Titration

in the preceding paragraph, titrate the solution, observing the resistance at two points prior to the stoichiometric point and at two points following the stoichiometric point. Construct the curve for the titration and locate the end point. Carry out the determination in triplicate. On a separate portion of the sample carry out a determination of moisture. A constant temperature oven operating in the range 105°–110° may be used. On the basis of the titrations and the results of the moisture determination, calculate the per cent of KCl in the sample on the dry basis.

[11] M. Dole, see reference given in § 11.
[12] Getman and Daniels, see reference given in § 11.

494. Examples.

1. In determining the pH of a solution of HCl at 25° by means of a hydrogen indicator electrode and a normal hydrogen reference electrode, it was observed that the reference electrode was positive with respect to the indicator electrode to the extent of 0.1182 volts. Calculate the pH of the solution. Calculate the hydrogen ion concentration of the solution.

2. In determining the pH of a solution at 25° by means of a hydrogen indicator electrode and a saturated calomel reference electrode, it was observed that the reference electrode was positive with respect to the indicator electrode to the extent of 0.3730 volts. Calculate the pH of the solution.

3. In determining the pH of a solution at 25° by means of a hydrogen indicator electrode and a saturated calomel reference electrode, the indicator electrode was found to be negative with respect to the reference electrode to the extent of 0.2380 volts. Calculate the pH of the solution.

4. In determining the pH of a solution at 25° by means of a quinhydrone indicator electrode and a saturated calomel reference electrode, the indicator electrode was found to be positive with respect to the reference electrode to the extent of 0.3020 volts. Calculate the pH of the solution.

5. In determining the pH of a solution at 25° by means of a glass electrode and a suitable reference electrode, the glass electrode was found to be negative with respect to the reference electrode to the extent of 0.519 volts. The difference of potential between these electrodes in a solution having a pH of 4.12 was 0.274 volts. Calculate the pH of the unknown solution.

6. In determining $e°$ for a glass electrode at 25°, a saturated calomel electrode and the glass electrode were inserted in a solution having a pH of 3. It was found that the glass electrode was positive with respect to the reference electrode to the extent of 0.2733 volts. Calculate $e°$ for the glass electrode.

7. In determining the pH of a solution at 25° by means of a glass indicator electrode and a saturated calomel electrode, it was found that the indicator electrode was positive with respect to the reference electrode to the extent of 0.2080 volts. The molar potential of the glass electrode is 0.6921 volts. Calculate the pH of the solution.

8. In the electrometric determination of Cr in an alloy of Ni, Mn, Fe and Cr, 0.6317 g. of sample was taken, the Cr oxidized to chromate ion by permanganate ion in sulphuric acid solution and then titrated electrometrically with 0.08632 M FeSO$_4$ using the combination: Hg|HgClsat. KCl|sat. KCl (Cr solution) Pt. The temperature was 27° and the following readings were obtained on 1/5th aliquots:

Aliquot 1		Aliquot 2	
ml. $FeSO_4$ added	E.M.F. obs. volts	ml. $FeSO_4$ added	E.M.F. obs. volts
0.00	0.7308	0.00	not read
2.00	.7194	6.90	0.7044
4.00	.7160	7.90	.6949
6.00	.7067	8.10	.7015
7.00	.7045	8.40	.7063
7.50	.6963	8.70	.6958*
8.00	.6936	9.00	.6514
8.30	.6918	9.30	.6306
8.60	.6833*	9.60	.5355
8.90	.6780	9.90	.5178
9.20	.6508	10.20	.5079
9.50	.5670		
9.80	.5286		
10.10	.5150		
10.40	.5063		

* Yellow color gone from solution.

What were the percentages of Cr on the whole sample corresponding to aliquots 1 and 2 ?

Suggestion Plot the results and locate the points of inflection.

9. In the titration of ferrous ion with ceric ion at 25°, using a saturated calomel reference electrode, calculate the potentiometer reading at the stoichiometric point.

10. Explain briefly the important features of a *differential potentiometric titration*. See D. A. MacInnes, "The Principles of Electrochemistry," p. 306, Reinhold Publishing Corp., New York, 1939.

11. Explain briefly the important features of a *Dead-stop end point* titration. See Kolthoff and Furman, "Potentiometric Titrations," p. 122 of reference given in § 11.

CHAPTER XXV

495. Introduction. — It has long been known that most substances, when viewed in daylight or in artificial light, exhibit what we ordinarily speak of as color, and that certain substances, when dissolved in a liquid, impart a characteristic color to the solution, while still other substances, which are insoluble in a liquid, produce turbidity when in a fine enough state of dispersion. It has more recently been known that the elements themselves, separately or in combination, when heated sufficiently high give off radiation (emission spectra) which is characteristic of the element or elements present.

The main purpose of this chapter is to acquaint the student with certain of the fundamental principles of light and color and of their measurement so as to help him to understand more clearly the use of the optical methods which employ a constant source of light and which find application in the domain of analytical chemistry. The advantage of such methods lies in the fact that we are able to determine with fair accuracy and ease very minute amounts of constituents; amounts ranging from several milligrams down to several micrograms, an accomplishment not easily attained, if at all, by other quantitative methods.

496. Color. — Since the province of chemical photometric analysis is to study the light effects caused by a given mass of substance under prescribed conditions, it becomes at once necessary to specify color in terms of a definite set of physical measurements.

The term *color* is used in science in three different senses:

1. By physiologists and psychologists, to denote a sensation aroused as a specific response to stimulation of the eye and its

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[1] "Handbook of Colorimetry" by A. Hardy, *et al.* has been found of invaluable assistance in developing much of the theoretical discussion in this chapter. For reference see § 11.

attached nervous mechanisms by radiant energy of certain wave lengths and intensities.

2. By physicists, to give a description to certain phenomena in the field of optics.

3. By chemists, to signify that which is used to give color: a pigment or dye, coloring matter.

Sources of Illumination. — The visual stimulation that results when one looks at a colored surface or object depends upon the character of the light that enters the eye from the surface or object, and this, in turn, depends upon the character of the light that initially illuminates the surface or object. By character we shall mean the composition of the light in terms of its component wave lengths (quality) along with the relative intensities of its respective wave lengths. The light that we shall consider first is daylight.

497. Daylight Wave Lengths. — When daylight is passed through a prism it is resolved into six broad bands, the visible spectrum, consisting of violet, blue, green, yellow, orange and red. If now each band is further resolved by means of a diffraction grating, it is found that the physical difference between the several regions is merely one of the wave length of light, and that the wave length varies continuously from one end of the spectrum to the other. The unit of length that is employed for specifying the wave length of visible radiation is the millimicron, $m\mu$ (1 millimicron = 10^{-7} cm.), and the visible spectrum range is about 400–700 $m\mu$ with the six broad spectral regions placed about as follows:

Spectral Region	Violet	Blue	Green	Yellow	Orange	Red
Range in millimicrons	400–450	450–500	500–570	570–590	590–610	610–700

498. Intensity. — In addition to the wave lengths themselves, we have to consider the intensities of the wave lengths, where, by intensity, we shall mean the number of ergs of heat generated per second by a beam of given wave length within a spectral band one millimicron in width and of cross section of 1 sq. cm. falling normally upon a sensitive temperature measuring device (thermo-pile) the surface of which has been blackened so as to convert the light energy into heat. The intensities are also expressed in terms of relative values on such a scale that the energy of the beam of

560 mμ is arbitrarily made equal to 100. Figure 116 shows the relative intensity of mean noon sunlight at Washington. From this it can be seen that daylight is a mixture of all the components of the visible spectrum in nearly equal proportions.
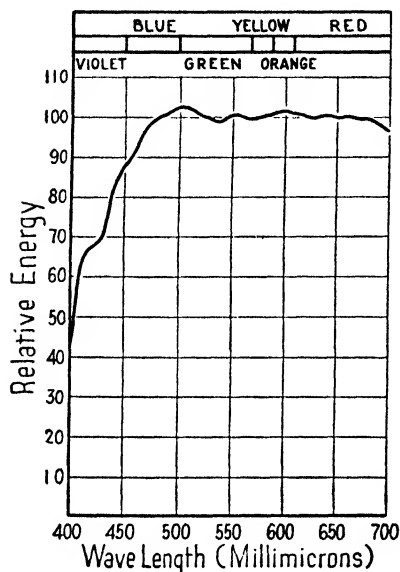
Fig. 116

Relative Intensity of Sunlight

499. White, Gray or Neutral Light. — When heterogeneous light arises from an intensity distribution among the wave lengths which is nearly (but not exactly) in equal proportions, it is called white, gray or neutral light. Daylight, as already shown, is of this type, but, owing to the fact that the actual intensities are subject to great variations due to the time of day and weather conditions, it is not suitable as a working source and, consequently, there have been developed several sources of artificial light which, when passed through suitable filters, give gray light of extreme constancy. See § 503.

The sun, as a light source, is illustrative of an incandescent solid. It is found that the radiation from an incandescent solid is practically independent of the material of which it is composed and depends only on its temperature; furthermore, the spectrum is continuous.[2]

500. Black Body Radiator. — The most efficient source of incandescence is the so-called *Black Body Radiator*, which gives off radiation of which the relative intensities depend only on the temperature of the body. Experimentally, a very close approach

[2] It is to be noted that the sun's spectrum, when resolved with a sufficiently fine diffraction grating, shows numerous dark bands (the Fraunhofer lines). These dark bands result from the absorption of certain wave lengths of the sun's radiation as it passes through the sun's atmosphere.

to ideal black body radiation is realized in the radiation from a small opening in a large cavity the walls of which are maintained at a constant temperature. The spectrum of black body radiation is continuous and the spectral energy distribution is given by Planck's Law (1900):

$$E = \frac{C_1 \lambda^{-5}}{e^{\frac{C_2}{\lambda T}} - 1}, \qquad (1)$$

where E is the amount of energy radiated in ergs per second per square centimeter of surface within a spectral band one millimicron in

Fig. 117

Energy Radiated by a Black Body

width, C_1 is a constant whose value is 3.70×10^{23}, e is the base of the natural system of logarithms, C_2 is a constant whose value is 1.433×10^7, λ is the wave length of light in millimicrons, and T is the absolute or Kelvin temperature of the body.

Fig. 118

Relative Energy Distribution from a Black Body

If we plot the energy radiated by a black body in the interval from 559.5 mμ to 560.5 mμ, as a function of temperature we get the graph shown in Figure 117 where both coördinates are logarithmic.

The relative distribution of energy from a black body at various temperatures is given in Figure 118.

501. Gray Body Radiators. — The energy radiated by many incandescent solids can be expressed by an equation similar to (1) differing only by the insertion of a constant ϵ, which is known as the emissivity:

$$E = \frac{\epsilon C_1 \lambda^{-5}}{e^{\frac{C_2}{\lambda T}} - 1}.\tag{2}$$

A tungsten filament, for example, has an emissivity of approximately 0.3 at the ordinary operating temperature of tungsten lamps. This means that a tungsten filament radiates only about 3/10 as much energy at every wave length as a black body at the same temperature. This proportional reduction in the emission affects only the quantity of radiation and not the quality. Materials whose spectral distribution of energy can be represented by the above equation are known as *Gray Body Radiators*. The standard Illuminant A described in § 503 is a gray body radiator.
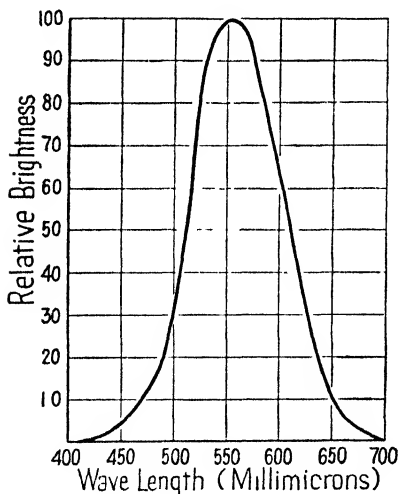
502. Relative Brightness, or Relative Visibility. — Relative brightness is the ratio of the brightness or visibility of a ray of given wave length to that of wave length 555 mμ, where each has the same intensity as measured in heat energy units (ergs/sec./cm.^{2}). The wave length of 555 mμ is selected because, of all the wave lengths, it has the maximum brightness for any given intensity. The relative brightness of the various wave lengths, 400 to 700 mμ, is given in Table 69 and Figure 119.[3]

Fig. 119

Relative Brightness of Visible Wave Lengths

[3] See "International Critical Tables," 1st ed., V, p. 436, 1929.

Table 69

RELATIVE BRIGHTNESS OF VISIBLE WAVE LENGTHS

Wave Length in Millimicrons	Relative Brightness	Wave Length in Millimicrons	Relative Brightness
400	0 04%	580	87 0%
410	12	590	75 7
420	40	600	63 1
430	1 16	610	50 3
440	2 3	620	38 1
450	3 8	630	26 5
460	6 0	640	17 5
470	9 1	650	10 7
480	13 9	660	6 1
490	20 8	670	3 2
500	32 3	680	1 7
510	50 3	690	0 82
520	71 0	700	41
530	86 2	710	21
540	95 4	720	.105
550	99 5	730	052
555	100 0	740	025
560	99 5	750	012
570	95 2	760	006

503. Standard Illuminants. — In 1931 the International Commission on Illumination adopted three light sources which can be easily reproduced. These sources are known as I. C. I. Illuminants A, B and C.

Illuminant A is a tungsten lamp, A, operated at a temperature of 2848° K. Suitable lamps that have been properly aged and calibrated are obtainable from the National Bureau of Standards, which also furnishes the operating data and characteristics of each lamp. The relative distribution of energy in the radiation from I. C. I. Illuminant A is given in Figure 120.

Illuminant B uses a lamp having the same spectral quality of Illuminant A in conjunction with a filter. The filter consists of a layer, one centimeter thick, of each of the solutions B_1 and B_2, these solutions being contained in a double cell constructed of white optical glass. The composition of each solution is as follows:

Solution B_1

Copper sulfate ($CuSO_4 \cdot 5H_2O$)	2.452 g.
Mannite ($C_6H_8(OH)_6$)	2.452 g.
Pyridine (C_5H_5N)	30.0 ml.
Distilled water to make	1000.0 ml.
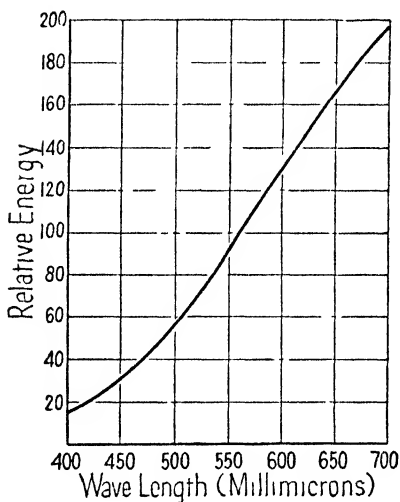
Fig. 120

Relative Energy Distribution of I. C. I. Illuminant A

Solution B_2

Cobalt-ammonium sulfate	
($CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$)	21.71 g.
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	16.11 g.
Sulfuric acid (density 1.835)	10.0 ml.
Distilled water to make	1000.0 ml.

Illuminant C likewise uses a lamp having the same spectral quality of Illuminant A in conjunction with a filter. An identical cell is used, but the solutions, C_1 and C_2, have the following compositions:

[612]

Solution C_1

Copper sulfate ($CuSO_4 \cdot 5H_2O$)	3 112 g.
Mannite ($C_6H_8(OH)_6$)	3.112 g
Pyridine (C_5H_5N)	30 0 ml.
Distilled water to make	1000.0 ml.

Solution C_2

Cobalt-ammonium sulfate	
($CoSO_4(NH_4)_2SO_4 \cdot 6H_2O$)	30.580 g.
Copper sulfate ($CuSO_4 \cdot 5H_2O$)	22.520 g.
Sulfuric acid (density 1.835)	10 0 ml.
Distilled water to make	1000 0 ml

The relative distribution of energy in the radiation from I. C. I. Illuminant C is given in Figure 121.
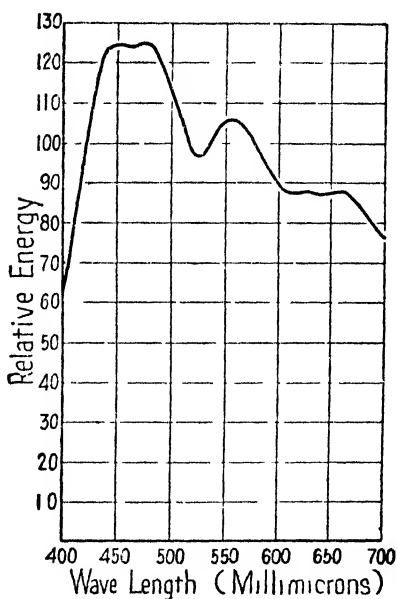
Fig. 121

Relative Energy Distribution of I. C. I. Illuminant C

504. Other Illuminants. — The radiation from mercury vapor gives several strong groups of lines.[4] The wave lengths of these, expressed in mμ, are as follows:

Yellow	79.1	577.0
Green	46.1	
Blue	35.8	434.8	433.9
Violet	07.9	404.7
Near ultraviolet	366.3 3	366.2 8	365.5	365.0

In addition to the above lines, the pair of sodium lines ($\lambda = 589.0$ mμ, $\lambda = 589.6$ mμ), isolated by appropriate filters, have been extensively used.

505. Spectral or Light Filters. — There are several types of filters, those of colored glass, dyed films of gelatin, colored solutions of water and of various organic solvents. By means of a suitable

Table 70

SPECTRAL FILTERS

Spectrum Filter	Range in mμ at		Maximum Transmission in mμ	Effective Filter Gravity in mμ	Effective Range in mμ		Transmission at Filter Gravity in %
	$\frac{1}{2}$	1/10			$\frac{1}{2}$	1/10	
S 75	..	..	...	750	40	..	26
S 72	..	..	...	729	31	68	38
S 66, 6/3.5	..	..	679	666	35	65	0.65
S 61	24	66	620	619	19	40	0.08
S 57	19	38	572	572	18	36	0.14
S 55, 0/1.7	17	28	551	550	17	29	0.36
S 53	20	35	528	530	20	35	1.45
S 50	26	46	488	494	26	44	0.55
S 47	25	44	458	463	24	42	5.0
S 45, 0/2.0	19	33	445	450	20	33	3.9
S 43	..	..	...	434	20	41	1.1

[4] The intensity of these lines as a function of lamp wattage has been carefully investigated by R. Küsh and G. Retschinsky, *Ann. Physik.* **20**, 563 (1906); G. S. Forbes and G. Harrison, *J. Am. Chem. Soc.*, **47**, 2449 (1925); L. Reeve, *J. Phys. Chem.*, **50**, 1427 (1926).

choice of these it is possible to isolate any one of many narrow spectral regions.[5]　As an illustration, we list herewith in Table 70 the spectral filters of colored glass put out by the firm of Carl Zeiss, Jena, to go with the Pulfrich Photometer.

506. Spectrophotometry. — When light (monochromatic or heterogeneous) falls on an object, a portion of the incident light is reflected, a portion of the light is absorbed within the material, and the remainder is transmitted.　It follows that

$$I_o = I_r + I_a + I_t$$

where I_o, I_r, I_a and I_t are the incident, reflected, absorbed and transmitted rays respectively.　Objects are said to be opaque when the transmitted portion is so small as to be negligible; when the transmitted portion is too large to be disregarded, the object is said to be transparent.　It is to be noted that transparent objects never have a negligible *reflection factor*, namely, $\frac{I_r}{I_o}$; thus a piece of clear white optical glass reflects about 8%, absorbs a fraction of 1% and transmits about 92% for thickness of 1.0 cm.

The measurements of the reflection factors, $\frac{I_r}{I_o}$, and the *transmission factors*, $\frac{I_t}{I_o}$, for given wave lengths of light, constitute the field of spectrophotometry.

507. Reflection Values. — Reflection values are of primary importance in studying the surfaces of opaque materials[6] but are only of interest to the quantitative analyst in so far as he needs to know the reflection losses which occur in the optical system that he is using.　Generally these will have to do with the air-glass interfaces consequent upon the use of glass cells, with respect to which it may be mentioned that every air-glass interface reflects approximately 4% of the light incident upon it.

The amount of light reflected at the interface between two different media may be calculated with adequate precision by

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[5] See "International Critical Tables," 1st. ed., V, p. 271, 1929.

[6] For further information in this regard, the reader is referred to the excellent treatment by A. Hardy *et al.* in "Handbook of Colorimetry," which is cited in § 11.

means of the special form of Fresnel's Law, for the case where monochromatic light strikes the interface normally. This expresses the intensity of the reflected light, I_r, in terms of the intensity of the incident light, I_0, and the respective refractive indices, n and n', by the relation

$$I_r = \left(\frac{n' - n}{n' + n}\right)^2 I_0.$$

The reflection loss, R, which is the ratio of I_r to I_0, thus becomes

$$R = \left(\frac{n' - n}{n' + n}\right)^2$$

For an air-glass interface where the refractive index of the glass is 1.5, $R = 0.04$. It should be mentioned that because of interface reflections, the transmission factor of two or more glasses in series is less than the product of their several transmission factors.

508. Transmission Factors; Determination by Means of Spectrophotometers. — Transparent materials, in an optical sense, may be either homogeneous or non-homogeneous. In the ordinary use of the terms, a homogeneous material would be called transparent, and a non-homogeneous material, translucent. The optical systems, namely the spectrophotometers, which are used to measure the intensity of the transmitted light in the case of a transparent material and that of a translucent material, are very similar with respect to their utilization of the incident light but differ radically as to the principle and method of measuring the subsequent intensity of the transmitted light.

509. Transmission Factors of Optically Homogeneous Materials. Transparent Solids. — For transparent solids the principle upon which the spectrophotometers[7] are based is essentially as follows. Light from a suitable source is dispersed into its spectral components. A nearly monochromatic beam of a known average wave length is then isolated, and divided by suitable means into two beams of equal intensity. One beam is passed through the

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[7] The student is referred to the work of F. Twyman and C. B. Allsopp, "The Practice of Absorption Spectrophotometry with Hilger Instruments," 2 ed.. Adam Hilger, Ltd., London, 1934.

test sample, the other beam is not; thus, there results an in-
equality of intensities of the two beams.   To make the intensities
equal, that of the comparison beam is diminished by the use of an
adjustable diaphragm or equivalent device.   The ratio of the final
intensity of the comparison beam to its initial intensity can then be
read directly from the calibrated scale of the instrument.   This
ratio is not the transmission factor because it includes the reflection
losses at the air-glass interfaces; in general, it will be less than the
transmission factor.   To correct for the reflection losses, we can
in many instances apply Fresnel's formula with sufficient precision,
in conjunction with Bouguer's (Lambert's) Law to be discussed in
§ 510.   The measurements are continued with monochromatic
light of other wave lengths selected at suitable distances apart,
from 400 mμ to 700 mμ, so as to give the entire visible spectrum.

510. Bouguer's (Lambert's) Law. — When monochromatic light
passes through a transparent medium, the rate of decrease of
intensity with the thickness of the medium is proportional to the
intensity of the light.   This observation was made by Bouguer in
1739 and again by Lambert in 1760.   This law, which is generally
referred to as Lambert's Law, may be expressed by a differential
equation:

$$-\frac{dI}{dl} = \kappa I, \tag{1}$$

where I and l represent intensity and thickness respectively.
This equation is easy to integrate because, upon rearranging, we
get

$$\frac{dI}{I} = -\kappa dl. \tag{2}$$

Integrating,

$$lnI = -\kappa l + \text{Constant} \tag{3}$$

To evaluate the constant, we note that when $l = 0, I$, the intensity,
is equal to the initial intensity I_0, whence,

$$lnI_0 = \text{Constant} \tag{4}$$

Substituting this value for the constant in equation (3), we get

$$lnI_t - lnI_0 = -\kappa l \tag{5}$$

By recasting the left-hand member of (5) we get the logarithmic form of Bouguer's (Lambert's) Law,

$$ln\frac{I_t}{I_0} = -\kappa l.$$ (6)

Changing (6) to the exponential form,

$$\frac{I_t}{I_0} = e^{-\kappa l}$$ (7)

where I_0 is the intensity of the monochromatic light falling upon a transparent medium of thickness l, I_t is the intensity of the light after passing through the medium, e is the natural (Naperian) base of logarithms,[8] and κ is a constant called the absorption coefficient.

Transmission Factor. — The value of the ratio I_t/I_0 is the transmission factor, T, of the sample for the thickness l and for the given wave length of light; the values of transmission factors are always less than unity.

The absorption coefficient, κ, is spoken of as a constant, but in reality it is a parameter, since it varies as we pass from one wave length of light to another in examining the same medium, and also varies as we pass from one medium to another using the same wave length of light.

511. Optical Density. — The optical density, d, of a medium, often spoken of simply as the density, is the Briggsian logarithm of the reciprocal of the transmission factor, namely

$$d = \log \frac{I_0}{I_t}$$

or if defined in exponential form

$$I_t = I_0 10^{-d}.$$

The term density was first introduced by Hurter and Driffield in connection with their studies on the blackening of photographic plates;[9] it is frequently used in specifying the results of spectro-photometric analyses of glasses and colored solutions.

[8] The value of e is 2.718 . . .
[9] *J. C. S. I.*, **9** May (1890).

512. Determination of the Absorption Coefficient, κ, for a Transparent Glass. — Using the data given in Table 71, obtained from an examination of various thicknesses of magenta glass with wave lengths of 460 mμ (blue), 590 mμ (yellow), 680 mμ (red),

Table 71[10]

TRANSMISSION FACTORS FOR A MAGENTA GLASS

Thickness of Glass in Centimeters	Transmission Factor for Wave Length of Light		
	460 mμ (blue)	590 mμ (yellow)	680 mμ (red)
0 10	0.970	0.740	0.945
.20	940	.553	.893
.30	.913	.410	.845
.40	.885	.305	.800
.60	.835	.170	.715
.80	.785	.090	.635
1.20	.697	.030	.510

we shall first plot the results to appropriate scale; this will give us three curves, I, II, III, of the type $T = e^{-\kappa l}$, shown in Figure 122. Designating the respective values of κ, by κ_1, κ_2 and κ_3, we shall obtain their respective values arithmetically as illustrated herewith:[11]

$$T = e^{-\kappa_1 l}$$
$$\log T = -\kappa_1 l \log c$$
$$\log 0.970 = -\kappa_1(0.1)(0.4343)$$
$$9.9868 - 10 = -\kappa_1(0.04343)$$
$$-0.0132 = -\kappa_1(0.04343)$$
$$\kappa_1 = 0.304$$

[10] Adapted from A. Hardy *et al.* "Handbook of Colorimetry," p. 24; reference given in § 11.

[11] It would be much quicker, but not as instructive, at this juncture to plot the values from the transformation $lnT = -\kappa l$ and to select the best straight line to represent the points; the line would then give us the value of the desired κ.
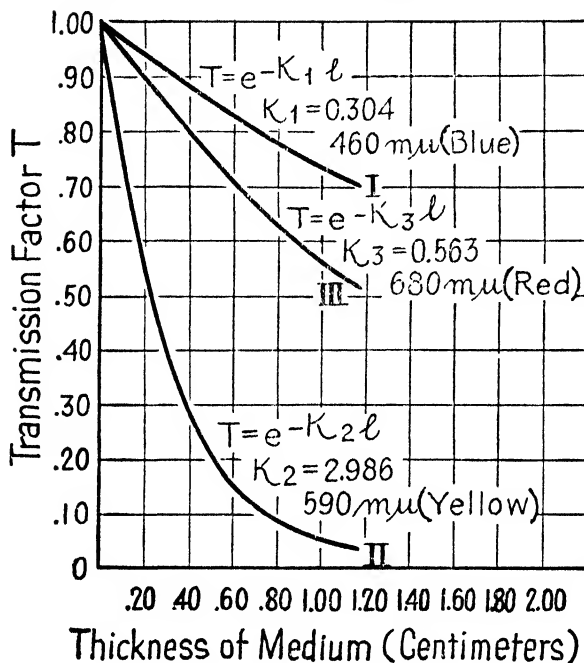
Fig. 122

Transmission Factors for a Magenta Glass

Proceeding in this manner, we get the values for κ_1, κ_2 and κ_3 listed below in Table 72:

Table 72

ABSORPTION COEFFICIENTS FOR A MAGENTA GLASS

Thickness of Glass in Centimeters	Absorption Coefficients		
	κ_1	κ_2	κ_3
0.10	0.304	3.012	0.567
.20	.310	2.962	.565
.30	.303	2.978	.561
.40	.310	2.975	.558
.60	.300	2.955	'.559
.80	.302	3.008	.567
1.20	.301	3.010	.561
Average	0.304	2.986	0.563

513. Transparent Liquids and Solutions. — If the sample to be examined is a liquid or solution, it is necessary that it be contained in a glass cell; glass cells for this purpose are made of optical glass and have the shape of a cube or rectangular parallelepiped. The introduction of the cell into a beam of light produces several effects:

1. The faces through which the beam passes may absorb an amount of light which is not negligible.

2. The two air-glass interfaces each reflect about 4% of the light incident upon them.

3. The solvent (in contradistinction to the dissolved solute) may absorb an amount of light which is not negligible.

In order to correct for these effects, it is better practice to have the comparison beam pass through a similar cell filled with the solvent only, as represented in the diagram of a Pulfrich photometer shown in Figure 131. When the intensity of the comparison beam is made equal to the intensity of the beam through the sample, the ratio of this intensity to the initial intensity of the comparison beam will be the transmission factor.

514. Beer's Law. — If we have several solutions, $S_1, S_2, S_3, \ldots$, made up of the same solvent and solute but having the solute in different concentrations, $c_1, c_2, c_3, \ldots$, then it follows from Bouguer's (Lambert's) Law, that for each solution we shall have transmission factors T corresponding to the absorption coefficients $\kappa_1, \kappa_2, \kappa_3, \ldots$, as given by the relationships:

$$T_{\text{ for } c_1} = e^{-\kappa_1 l}$$
$$T_{\text{ for } c_2} = e^{-\kappa_2 l}$$
$$T_{\text{ for } c_3} = e^{-\kappa_3 l}$$

or, using the common base 10 instead of the natural base e to express the relationship, we get,

$$T_{\text{ for } c_1} = 10^{-K_1 l}$$
$$T_{\text{ for } c_2} = 10^{-K_2 l}$$
$$T_{\text{ for } c_3} = 10^{-K_3 l}$$

where, of course, $K = 0.4343\,\kappa$.

Extinction Coefficient. — The exponent K when 10 is used as base is called the extinction coefficient.

Molecular Extinction Coefficient. — We can consider in the case of any given solution with a single solute that the extinction coefficient K is resolvable into factors, c, the concentration of the solute and ϵ the quotient of K divided by c. We may then replace K by its equivalent ϵc and our relationship becomes

$$T = 10^{-\epsilon cl}.$$

If c is expressed in moles per liter and l in centimeters then ϵ is known as the molecular extinction coefficient.

Beer showed that the absorption coefficients K_1, K_2, K_3, . . ., are related to the concentrations c_1, c_2, c_3, ... For some solutions the relationship is linear, that is to say, K is directly proportional to c, thus,

$$K = ac$$

where a is a constant.

For other solutions, and these constitute the majority of cases, the relationship is non-linear, and we have

$$K = \phi c$$

where ϕ is a variable and where it is to be noted that the variation of ϕ with c must be found by experiment.

515. Application of Beer's Law; Case I. — In Case I K is proportional to c. Let us consider the work of A. Hantsch[12] on solutions of potassium chromate in water containing small concentrations of potassium hydroxide to minimize the hydrolysis,

$$2 \, CrO_4^- + H_2O \rightarrow Cr_2O_7^- + 2OH^-.$$
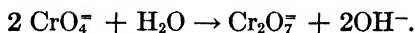
The measurements of the transmission factors were made with the mercury blue line ($\lambda = 436 \, m\mu$). The results are given herewith in Table 73. From the values in the fifth column, it is at once evident that K is proportional to c, and we can write

$$K = ac \qquad (1)$$

where a is a constant with the value 315.

[12] A. Hantsch, *Z. physik. Chem.*, **72**, 366 (1910).

Table 73

TRANSMISSION FACTORS FOR SODIUM CHROMATE SOLUTIONS

Conc. of Na_2CrO_4 Moles per Liter	Depth of Column in cm.	Transmission Factor	Absorption Coefficient K*	Ratio of K to c
0.0002	12.0	0.176	0.0630	315
.001	2.0	.238	.3105	311
.002	1.0	.234	.630	315
.01	.20	.234	3.15	315
.02	.10	.234	6.30	315
			Average	314.8

* K is obtained from equation $T = 10^{-Kl}$ where l is given in cm.

Plotting the transmission factors for $c_1 = 0.0002\,M$ and $c_2 = 0.0006\,M$, we get the curves A and B of Figure 123.
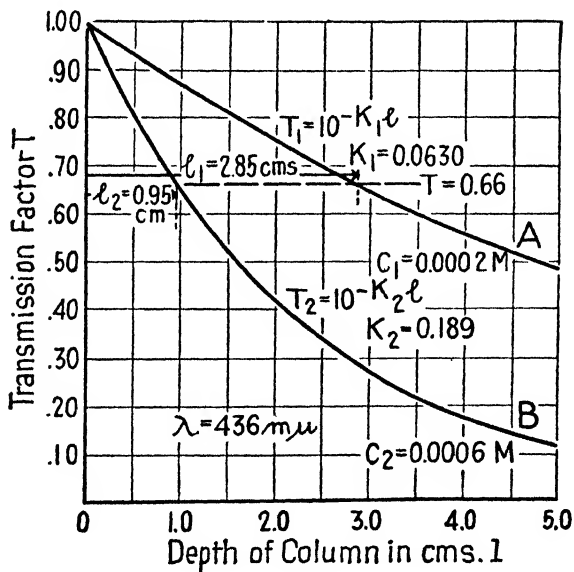
Fig. 123

Transmission Factors for Sodium Chromate Solutions

If we fix our attention on the same transmission factor for each curve, say $T = 0.66$, we notice that the respective thicknesses of column are

$$l_1 = 2.85 \text{ cm.} \tag{2}$$

$$l_2 = 0.95 \text{ cm.} \tag{3}$$

By virtue of the analytic expressions for the two curves A and B,

$$T_A = 10^{-K_1 l_1} \tag{4}$$

$$T_B = 10^{-K_2 l_2}, \tag{5}$$

we have for equal values of T_A and T_B that

$$\frac{l_1}{l_2} = \frac{K_2}{K_1}. \tag{6}$$

Substituting for K_1 and K_2 their values in terms of c_1 and c_2 from (1) namely, $K_1 = ac_1$, $K_2 = ac_2$, we get

$$\frac{l_1}{l_2} = \frac{ac_2}{ac_1} \tag{7}$$

or, since a is a constant, we may cancel it out, obtaining

$$\frac{l_1}{l_2} = \frac{c_2}{c_1}. \tag{8}$$

Putting numerical values in (8) as a verification, we obtain the identity,

$$\frac{2.85}{0.95} = \frac{0.0006}{0.0002}.$$

Equation (8) expresses the essence of Beer's Law, namely: If we have two solutions S_1 and S_2, made up of the same solvent and solute but having the solute in different concentrations c_1 and c_2, and if the absorption coefficients for monochromatic light of designated wave length λ are K_1 and K_2, and the K's are proportional to the c's, then, for equal transmission factors, the ratio of the respective thicknesses of columns l_1 and l_2 will be inversely proportional to the concentrations c_1 and c_2.

516. Application of Beer's Law; Case II. — In Case II, K is a non-linear function of c. For our example let us take the results of Hantsch[13] on aqueous solutions of potassium dichromate; the light

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[13] A. Hantsch, Z. physik. Chem., 72, 336 (1910).

used was the mercury blue, $\lambda = 436$. The results are given in Table 74.

Table 74

ABSORPTION COEFFICIENTS FOR POTASSIUM DICHROMATE SOLUTIONS

Conc. of $K_2Cr_2O_7$ in Equivalents per Liter	Absorption Coefficient K	Ratio of K to c
0.0001	0.0222	222
.0002	.0444	222
.0005	.1120	224
.001	.227	227
.002	.456	228
.00333	.763	229
.005	1.175	235
.01	2.47	247
.02	5.06	253
.04	10.28	257

From the above table it is readily seen that K is not proportional to c; and that if we put

$$K = \phi c \qquad (\phi \text{ a variable}) \qquad (9)$$

ϕ varies from 222 to 257 as c varies from 0.0001 to 0.04 N.

Plotting the transmission factors for concentrations $c_1 = 0.0002$ and $c_2 = 0.0006$ with corresponding absorption coefficients, $K_1 = 0.0444$ and $K_2 = 0.1348$, we get the graphs C and D of Figure 124.

If we fix our attention on the same transmission factor for each curve, say $T = 0.76$, we notice that the respective thicknesses of column are:

$$l_1 = 2.68 \text{ cm.}$$
$$l_2 = 0.882 \text{ cm.}$$

As already shown (6), for equal value of T_C and T_D, we have

$$\frac{l_1}{l_2} = \frac{K_2}{K_1}.$$

Substituting for K_1 and K_2 their values in terms of c_1 and c_2 from (9), we get

$$\frac{l_1}{l_2} = \frac{\phi_2 c_2}{\phi_1 c_1},$$

which shows that the ratio of the respective thicknesses of columns is different from the inverse ratio of the concentrations by the
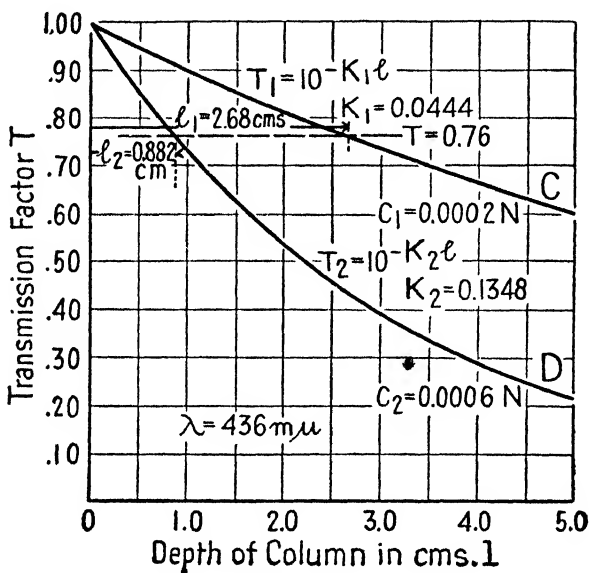
Fig. 124

Transmission Factors for Potassium Dichromate Solutions

ratio of ϕ_2/ϕ_1. The value of this last ratio is found to be $\frac{224.6}{222.0}$ or 1.012, whence we have

$$\frac{l_1}{l_2} = 1.012 \frac{c_2}{c_1}.$$

Putting in numerical values as a verification, we obtain the identity

$$\frac{2.68}{0.882} = 3.035 = 1.012 \frac{0.0006}{0.0002}.$$

In many cases where K is a non-linear function of c, the ratios of ϕ_2/ϕ_1 are considerably larger than illustrated above. The departure of the ratio ϕ_2/ϕ_1 from unity in any given case represents the departure of Beer's Law from ideality.

517. *Further Application of Beer's Law.* — If we examine Bouguer's (Lambert's) Law in the form

$$T = 10^{-Kl},$$

we notice that, if $l = 1$ cm., then

$$- \log T = K.$$

Hence, if we use 1 cm. of column of solution and determine the transmission factor, then, the negative logarithm of the transmission factor gives at once the value of the absorption coefficient; thus we have the correspondence shown by the values in Table 75 and by the dual scale in Figure 125.

Table 75

Transmission Factor for 1 cm. T	Negative Logarithm of (T) Equals Absorption Coefficient K
1.00	0.000
.95	.022
.90	.046
.85	.071
.80	.097
.75	.125
.70	.155
.65	.187
.60	.222
.55	.260
.50	.301
.45	.347
.40	.398
.35	.456
.30	.523
.25	.602
.20	.699
.15	.824
.10	1.000
.08	1.099
.06	1.222
.04	1.398
.02	1.699
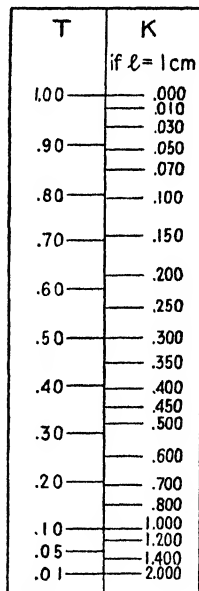
Fig. 125

If, instead of 1 cm. of column, we use l cm. and determine the transmission factor, then the readings of the K column must be divided by l; this follows from the fact that K in general is equal to the quotient of the negative log of T by l:

$$T = 10^{-Kl}$$
$$-\log T = Kl$$
$$\frac{-\log T}{l} = K$$

518. Example Involving Beer's Law. — Suppose that we have an aqueous standard solution containing 9.49 mg. of uric acid per 100 ml. of solution, treated with phosphotungstic acid reagent by the method of L. Heilmeyer and W. Krebs[14] so as to develop a green color. If the transmission factor is determined using monochromatic light with wave length of 572 mμ and employing 1.0 cm. of column of solution, we find

Transmission factor = 0.10

$\therefore$ Absorption Coefficient = 1.000.

Suppose, next, that we have another solution of uric acid and that our problem is to find its content of uric acid. We develop the green color as we did with the standard sample, but this time we employ 2.0 cm. of column and find

Transmission factor = 0.501

$\therefore$ Absorption Coefficient = $\dfrac{0.300}{2}$ = 0.150.

Now, we also know in this case that Beer's Law is followed, whence,

$$K_1 : K_2 : : c_1 : c_2$$
$$1.00 : 0.150 : : 9.49 : x.$$

Solving for x, we get

$$x = 1.42 \text{ mg. per } 100 \text{ ml.}$$

519. Color from Daylight or Gray Light Illumination. — It will be remembered from § 497 that daylight is a mixture of all the rays of the visible spectrum (λ = 400 to 700 mμ) for which the

[14] L. Heilmeyer and W. Krebs, *Biochem. Z.*, **223**, 365 (1930).

component rays have very nearly the same relative intensities (as measured in heat energy units). When daylight passes through a transparent medium — solid, liquid, solution, or gas — each component ray will have its own specific coefficient of absorption; if all the coefficients are sensibly of the same order of magnitude, the rays will all be absorbed to about the same extent and the character of the emergent light will be the same as that of daylight; when light of such composition enters the eye, it produces no sensation of color and the body in such cases is said to be colorless; pure water is very nearly colorless.

Fig. 126

Transmission Factors for 0.05 M Copper Sulfate Solution

If the coefficients are of different orders of magnitude, the rays with the larger coefficients will be absorbed to a larger extent than those with the smaller, and the emergent light will be predominantly richer in those rays (as measured in heat energy

Fig. 127

Relative Brightness of the Transmitted Wave Lengths from 0.05 M Copper Sulfate Solution

units) which are least absorbed; when such light enters the eye, it produces the sensation of color and the body is said to be colored. The color sensation, however, is an integral effect of the respective stimuli of the various rays where the stimulus of any given ray is equal to the product of its emergent intensity by its relative visibility factor. As an example, let us take the case of a solution of 0.05 M copper sulfate[15]; its photometric analysis is given in Table 76 and portrayed graphically in Figures 126 and 127 which give the Transmission Factors and Relative Brightness respectively.

[15] Data adapted from "International Critical Tables," 1st ed., V, 330, 1929.

Table 76

PHOTOMETRIC ANALYSIS OF 0.05 M CuSO$_4$

Wave Length of Light in Millimicrons	Absorption Coefficient (base 10 l in cm.)	Transmission Factor for 1 cm.	Relative Brightness Factor	Relative Brightness
400	0.0995	0.795	0.04%	0.03%
420	.0400	.912	.40	.36
440	.0224	.949	2.3	2.18
460	.0126	.971	6.0	5.82
480	.00885	.980	13.9	13.6
500	.00885	.980	32.3	31.7
520	.0126	.971	71.0	69.0
540	.0224	.949	95.4	90.5
560	.0446	.902	99.5	89.6
580	.126	.748	87.0	65.1
600	.354	.443	63.1	27.9
620	.795	.160	38.1	6.10
640	1.26	.055	17.5	.96
660	1.78	.0165	6.1	.10
680	2.51	.0031	1.7	.005
700	3.15	.0007	.41	.0002

520. Chromaticity. — Chromaticity is defined as that which characterizes a color without reference to its brilliance; a color having hue and saturation, as red, green, brown, etc. White, black and gray have no chromaticity. Chromaticity is also called chroma or colorimetric quality. A more detailed discussion of the subject of chromaticity is given in § 560 of the Appendix.

521. Photometric Methods. — The photometric methods which we shall consider all depend on a comparison of the emergent light from the unknown solution with that from a known solution. This comparison can be effected by means of methods involving one of the following:

1. Variation of concentration
2. Variation of depth of solution
3. Variation of a comparison light beam

Variation of Concentration Methods. — In methods involving variation in concentration, either the unknown solution or a standard solution is diluted until the emergent light from both is

the same when viewed through the same depth of solution. This can be accomplished in a number of ways, (a) by making a series of known solutions of varying concentration with which the unknown solution can be compared as described in determinations with Nessler tubes in §§ 525 to 531, (b) by adding carefully measured quantities of standard solution to the known solution until it matches the unknown solution, (c) by diluting either the known solution or the unknown solution until they match.

Variation of Depth Methods. — In methods involving variation in depth, the length of path of the light through either the unknown solution or the standard solution is varied until the emergent light from both appears the same. The Duboscq colorimeter described in § 532 makes use of this method.

Methods Involving Variation of Comparison Light Beam. — The method in which a comparison beam is varied is made use of in the Pulfrich photometer described in § 535. In this method the intensity of a comparison beam is varied to match the emergent beam from a known sample. It is then varied to match the emergent beam from the unknown sample. From the intensities of the comparison beams and emergent beams the transmission factors, and extinction coefficients of the known and unknown solutions and the concentration of the unknown solution can be determined.

Many photometric methods possess the advantage over gravimetric or volumetric methods of requiring much less time. Since a high degree of precision is not possible in comparing solutions in which the concentration of the colored substance is great, photometric methods are necessarily limited to the analysis of small samples or samples in which the percentage of the constituent being determined is small. The accuracy of photometric methods is usually not as high as that which is obtainable in most gravimetric and volumetric methods in which the weight of the constituent being determined is relatively large. Photometric methods compare favorably, however, with other methods with respect to accuracy when the weight of constituent being determined is small.

522. Instruments and Their Use for Transparent Media. — The types of instrument employed to measure the color (transmitted light) of transparent media or materials are relatively few,

although there are numerous varieties under each type. The types are:

1. Colorimeters
2. Gradation Photometers
3. Spectrophotometers

523. Colorimeters. — Colorimeters are instruments or devices for determining and specifying colors by comparison with other colors or with complex stimuli not in general identical with the actual stimulus. They differ from gradation photometers and spectrophotometers, which measure and specify the energy distribution of the transmitted light evoking the color. They give results not independent of abnormalities in the observer's color vision. We shall mention just two forms of colorimeter: (1) glass cylinders of standardized dimensions, and (2) the Duboscq colorimeter. For further information, of which there is a great wealth, the student is referred to Yoe's work on colorimetry. (See § 11.)

524. Glass Cylinders of Standardized Dimensions. — Glass cylinders of standard dimensions are generally used in sets, the individual cylinders of a set being filled to the same depth with solutions of progressive color intensities to form a standard series against which the color intensity of the sample under examination is matched visually. Glass cylinders used in this manner constitute the simplest form of colorimeter. The dimensions of the several types of cylinders that are used (Eggertz tubes, Nessler tubes, etc.) differ with respect to the type, but the dimensions of the cylinders of any particular type must agree within close tolerances. We shall describe the Nessler tubes, since these are probably the most widely used.

525. Nessler Tubes. — Nessler tubes are made of clear glass of uniform bore and with polished flat bottoms. There are two sizes, 50 ml. and 100 ml., with specifications as follows:

Capacity ml.	Overall height mm.	Height to mark mm.
50	250	210 ± 6
100	300	260 ± 6

In using the tubes, the procedure is to arrange a suitable number in a rack and then to introduce into one tube after the other

measured and progressive amounts of a standardized (usually very dilute) solution containing the constituent that is to be determined in the unknown sample.   To each tube is then added equal amounts of solutions having known and appropriate concentrations of reagents in order to develop the color satisfactorily.   Then each solution is made up to the mark on the tube with distilled water and the contents are thoroughly mixed.

526. Exercise No. 62.   The Determination of Iron in Water by Means of Thiocyanate Ion.[16] -- Evaporate to dryness in an evaporating dish 100 ml. or less of the water to be tested.   If the water contains silt, this evaporation should be carried out in the presence of 5 to 10 ml. of 12 M hydrochloric acid.   If much organic matter is present, destroy it by ignition.   If the ignition is unduly prolonged, the iron in the sample may be difficult to dissolve.   If the sample was not ignited, heat sufficiently to drive off excess acid.

Cool the evaporating dish and add 1 ml. of 3 M hydrochloric acid.   Warm on the water bath, adding portions of distilled water to prevent the solution from being evaporated to dryness.   Rinse the hot solution into a 50 ml. Nessler tube, filtering if necessary.   Add 0.04 M KMnO$_4$ solution, a drop at a time, until the color of permanganate ion persists for at least 5 minutes.   Cool the solution and dilute to the mark with distilled water.   The sample is now ready to compare with standard solutions.

Standard Iron Solutions. — Prepare in advance a standard ferric solution by dissolving 0.7022 g. of crystallized ferrous ammonium sulfate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ in 50 ml. of distilled water and 20 ml. of 18 M sulfuric acid.   Warm the solution and add potassium permanganate until the iron is completely oxidized.   Dilute to one liter.   One milliliter of this solution will contain 0.1 mg. of Fe.

Place in matched Nessler tubes measured volumes of standard iron solution in sufficient amounts to produce a set of standards covering the range of the analysis at hand.   Dilute each solution to about 40 ml. and add 5 ml. of 3 M hydrochloric acid and 1 or 2 drops of 0.04 M potassium permanganate solution.   Dilute each

[16] The method given here is substantially that given by the American Public Health Association in "Standard Methods of Water Analysis," 7th ed., 1933.

solution to the mark. For the purpose of illustration, a series of standards is shown in Table 77.

Table 77

Tube Number	Known Amount of Constituent	Appropriate Amounts of Accompanying Reagents		Total Volume
1	0.02 mg Fe	5 ml. 0.2 M KCNS + 5 ml. 3 M HCl		50 ml.
2	.03 "	"	"	"
3	.04 "	"	"	"
4	.05 "	"	"	"
5	.06 "	"	"	"
6	.07 "	"	"	"
7	.08 "	"	"	"
8	.09 "	"	"	"
9	.10 "	"	"	"

Comparison. — To each of the standard solutions and to the unknown solution add 5 ml. of 0.2 M potassium thiocyanate solution and mix. Compare the color of the unknown solution with the appropriate tube of the series of standards or interpolate between two successive tubes. This comparison must be performed at once as the standard solutions are not permanent. As a result of the comparison, calculate the milligrams of Fe per liter of sample. The permanent color standards described in § 527 may be used in this determination.

527. Permanent Color Standards for the Determination of Iron. — Instead of preparing a set of color standards which must be made up fresh each time, it is possible to prepare permanent standards by employing varying mixtures of certain inorganic salt solutions. One of these solutions is prepared by dissolving 4 g. of K_2PtCl_6 in distilled water, adding 200 ml. of 12 M hydrochloric acid and diluting to 1 liter with distilled water. The other solution is prepared by dissolving 48 g. of $CoCl_2 \cdot 6H_2O$ in distilled water, adding 200 ml. of 12 M hydrochloric acid and diluting to 1 liter with distilled water. The volumes of platinum and cobalt solutions, given in Table 78, are then placed in Nessler tubes. Each solution is then made up to the 50 ml. mark with distilled water. The iron equivalents of these standards are shown in the first column.

Table 78

PERMANENT STANDARDS FOR THE DETERMINATION OF IRON

mgm. of Fe	ml. of Pt Solution	ml. of Co Solution
0.0	0.0	0.0
0 01	1.00	0.60
0.02	2.25	1.20
0.03	3.30	1.85
0.04	4.65	2.75
0.05	5.75	3.65
0.075	8.85	6.60
0.10	11.30	10.00
0.125	14.70	12.80
0.15	16.85	15.10

528. Exercise No. 63. The Determination of Iron in Water by Means of the Thiocyanate Ion and Permanent Color Standards. — Prepare the necessary color standards from cobalt and platinum solutions as described in § 527.

Prepare the unknown sample of water exactly as directed in § 526. Compare the color developed in the unknown with that of the appropriate permanent color standard or interpolate between two color standards. From the results of the comparison calculate the milligrams per liter of iron in the original sample.

529. Permanent Color Standards for Any Chromaticity. — It is possible to prepare permanent color standards of almost any chromaticity by employing varying mixtures of certain inorganic salt solutions. Thus, Arny and co-workers[17] have shown that very satisfactory standards for general use can be prepared by using the following combinations:

In dilute hydrochloric acid

Varying mix- ⌠copper chloride
tures of the | ferric chloride
same normal- | cobalt chloride
ity of   ⌡

In dilute ammonium hydroxide

Varying   ⌠
mixtures |
of the | copper chloride
same | potassium dichromate
normal- | cobalt chloride
ity of   ⌡

[17] H. V. Arny and C. H. Ring, *J. Franklin Inst.* **180**, 199 (1915); *J. Ind. Eng. Chem.* **8**, 309 (1916); H. V. Arny and A. Taub, *J. Am. Pharm. Assoc.* **12**, 839 (1923); A. Taub, *J. Am. Pharm. Assoc.* **16** (1917).

530. Permanent Standards for Ammonia Determination. — As another illustration of the use of permanent standards, we shall mention the use of platinum-cobalt standards in the colorimetric determination of very small amounts of ammonia in water.[18]   A 50 ml. sample of water should contain a concentration of NH_3 not over 1.6 mg. per liter.   It is treated with 2 ml. of Nessler's solution,[19] which is an alkaline solution of mercuric iodide in potassium iodide.   It is then allowed to stand for 10 minutes at room temperature in order that the reaction product, $NH_2Hg_2I_3$, which gives rise to an orange-brown color, may fully form.   The reaction is

$$2(HgI_2 \cdot 2KI) + 2NH_3 \rightarrow NH_2Hg_2I_3 + 4KI + NH_4I.$$
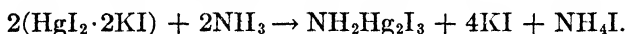
The color is matched against the platinum-cobalt standards, which previously have been standardized against a reference set of standards obtained by treating known amounts of ammonium chloride with Nessler's solution.

Reagents for Reference Standards. — The reagents used in preparing the reference standards are as follows:

1. Ammonia-free water.

2. Standard ammonium chloride solution; prepared by dissolving 3.82 g. of ammonium chloride in one liter of distilled water and diluting 10 ml. of this solution to one liter with ammonia-free water.   One milliliter equals 0.00001 g. of nitrogen.

3. Nessler's reagent; prepared by dissolving 50 g. of potassium iodide in a minimum quantity of cold water.   A saturated solution of mercuric chloride is added until a slight precipitate persists permanently.   A volume of 400 ml. of 50 per cent solution of potassium hydrate, made by dissolving potassium hydrate and allowing it to clarify by sedimentation before use, is added.   The solution is then diluted to one liter, allowed to settle, and decanted. This solution should give the required color with ammonia within five minutes after addition and should not precipitate with small amounts of ammonia within two hours.

Reference Standards. — A series of 16 Nessler tubes is prepared. These tubes should contain the following numbers of milliliters of

[18] American Public Health Association. Standard Methods of Water Analysis, Boston, 1915.

[19] J. Nessler, *Chem. Zentralbl.* **27** N. F. I. 529 (1856).

the standard ammonium chloride solution, diluted to 50 ml. with ammonia-free water, namely: 0.0, 0.1, 0.3, 0.5, 0.7, 1.0, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, 4.0, and 6.0. These will contain 0.00001 g. of nitrogen for each milliliter of the standard solution used.

The standards are then nesslerized by adding 2 ml. of Nessler's reagent to each tube. The contents of the tubes is not stirred since the reagent, having a density considerably greater than the solution, sinks rapidly through the solution. The tubes are allowed to stand for at least 10 minutes after nesslerizing. In comparing the colors produced in these tubes with the colors to be matched, the analyst should look vertically downward through the tubes at a white surface placed at an angle in front of a window so as to reflect the light upwards.

Preparation of Permanent Standards. — The solutions used in preparing platinum-cobalt standards are as follows:

1. Platinum Solution. — Two grams of potassium platinic chloride ($PtCl_4 \cdot 2KCl$) is weighed out and dissolved in a small amount of distilled water, 100 ml. of 1.2 M hydrochloric acid is added and the solution is made up to one liter.

2. Cobalt Solution. — Twelve grams of cobaltous chloride, ($CoCl_2 \cdot 6H_2O$), is weighed out and dissolved in distilled water, after which 100 ml. of 1.2 M hydrochloric acid is added and the solution is made up to one liter.

The standards are prepared by putting varying amounts of these two solutions into Nessler tubes and filling up to the 50 ml. mark with distilled water as shown in Table 79.

The amounts stated are approximate, but the actual amount necessary will vary with the character of the Nessler solution used, with the color sensitiveness of the analyst's eye, and with other incidental conditions. The final test of the standard is best obtained by comparing it with the reference standards and modifying the tint accordingly. Such a comparison should be made for each new batch of Nessler solution, and should be checked by each analyst. These standards may be kept for several months if protected from dust.

531. Exercise No. 64. Determination of Free Ammonia in Potable Water. — There are two methods for determining free ammonia in water, (A) by distillation, and (B) by direct nessleriza-

Table 79

PERMANENT STANDARDS FOR THE DETERMINATION OF AMMONIA

Equivalent Volume of Standard Ammonium Chloride ml.	Platinum Solution ml.	Cobalt Solution ml.
0.0	1.2	0.0
0.1	1.8	0.0
0.2	2.8	0.0
0.4	4.7	0.1
0.7	5.9	0.2
1.0	7.7	0.5
1.4	9.9	1.1
1.7	11.4	1.7
2.0	12.7	2.2
2.5	15.0	3.3
3.0	19.0	5.7
4.0	19.7	7.1
4.5	19.9	8.7
5.0	21.0	10.4
6.0	20.0	15.0
7.0	20.0	22.0

tion. The former is recommended for most waters, while the latter is preferable for sewages, sewage effluents, and highly polluted waters. We shall describe the distillation method.

Connect a metal or glass flask to a condenser having a tin or aluminum condenser tube, the condenser being conveniently arranged to deliver the distillate directly into the Nessler tubes. Free the apparatus from ammonia by boiling distilled water in the flask until the distillate shows no further traces of free ammonia. Then empty the distilling flask and measure into it 500 ml. of the sample (in this case, drinking water) or a smaller portion diluted to 500 ml. Heat so that the distillation will be at the rate of not more than 10 ml. per minute and not less then 6 ml. per minute.

Collect three Nessler tubes of the distillate, 50 ml. to each portion; these contain the free ammonia to be nesslerized. If the sample is acid, or if the presence of urea is suspected, add about 0.5 g. of sodium carbonate previous to distillation; omit this when possible, as it tends to increase bumping.

Nesslerize the distillates, as described in § 530 under Reference Standards, by adding 2 ml. of Nessler's reagent to each tube and allowing each to stand 10 minutes and then comparing with the

Permanent Standards.   After the readings have been made and recorded, add together the results obtained for each tube, and, from the total, calculate the amount of free ammonia in the sample taken for distillation, expressing the result as the "number of parts per million of nitrogen as free ammonia" in the sample.

532. Duboscq Colorimeter. — The Duboscq colorimeter was devised by Jules Duboscq in 1854, and, with certain improvements in construction, is one of the standard types of present day colorimeters; its optical diagram is given in Figure 128.

Light from daylight or from a filament bulb is reflected by means of a mirror M, which is mounted about a horizontal axis and has two reflecting surfaces — a plane silvered mirror and a plate of opal glass, the latter to reflect light diffusely.   The reflected light passes through two glass slits, the standard and unknown solutions S_1 and S_2 contained in the cups C_1 and C_2, then through the two glass plungers G_1 and G_2, the prism R and the eyepiece E.   An observer, in looking through the eyepiece, sees two semi-circular half-fields of view separated by a very fine line; the left half-field corresponds to the light passing through the right cup, the right half-field to the light passing through the left cup.   The glass plungers G_1 and G_2 are mounted permanently to the frame of the instrument in fixed positions, but the cups C_1 and C_2 are mounted on separate and movable platforms P_1 and P_2 and can be easily removed for purposes of filling and cleaning. By raising or lowering the heights of the platforms, usually accomplished by turning a thumb screw which operates a rack and pinion device, the depths of columns L_1 and L_2, through which the light passes, can be adjusted as desired, and in most instruments to a precision of 0.1 mm.   The respective
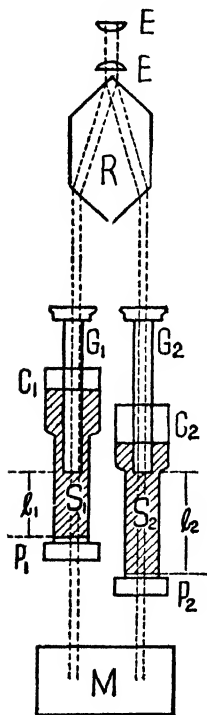
Fig. 128

Optical   Diagram of   the   Duboscq Colorimeter

readings are read from graduated scales with vernier attach-
ments (not shown in the figure). If Beer's Law is followed, then
we have for equal color intensities,

$$\frac{l_1}{l_2} = \frac{c_2}{c_1}$$

where c_1 represents the concentration of constituent in the solution
S_1, and c_2 has a similar significance for the solution S_2.

533. Use of the Duboscq Colorimeter. — *First*, each cup is
raised gently until its bottom just engages the bottom of the
plunger, then the respective verniers are read; these should each
read *zero*. If a reading is different from zero, the cup is lowered,
the screw of the plunger loosened, and the plunger pulled down
about a millimeter. Next, the cup is raised slowly until the
vernier registers zero; the set screw of the plunger is then tightened.
The cup and its plunger are now in proper adjustment.

Second, both cups are raised until each meets the bottom of its
plunger. The analyst should then look through the end piece and
move the reflector until both halves of the field appear equal.

Third, one of the cups, let us say the left cup, is filled with a
solution which has the same color and approximately the same
intensity as the unknown solution. We shall speak of this solution
as the *auxiliary solution*. The plunger is set near the middle of the
scale and is allowed to stay there throughout the whole deter-
mination.

The other cup is filled with the standard solution, the cup is
raised until equal color intensity is observed in the two halves of
the field, and the reading of the scale is recorded. This procedure
is repeated until five readings have been obtained by raising the
cup to establish the equi-intensity point; similarly, five readings
are obtained by lowering the cup to establish the equi-intensity
point. The average of all ten readings is then computed and
designated by L_s. The cup is then removed, its contents discarded,
and it is washed several times with water. It is then rinsed once
or twice with small portions of the unknown. Five readings are
obtained by raising the cup, and five readings by lowering the cup.
The average of all ten readings is computed and designated by L_u.
Assuming that Beer's Law holds, we have:

$$\frac{L_r}{L_u} = \frac{C_u}{C_s}$$

where C_s represents the concentration of the constituent in the standard solution, and C_u has a similar significance for the unknown.

534. Exercise No. 65. The Determination of Chromium as Chromate by Means of the Duboscq Colorimeter.[20] — Weigh out carefully about 5 g. of chromium steel. Transfer the sample to a flask and dissolve it in 50 ml. of 6 M hydrocholoric acid. Nearly neutralize the solution with 1.8 M sodium carbonate solution and then complete the neutralization with a 10% suspension of barium carbonate. Then add 10 ml. of barium carbonate suspension in excess. Boil gently for from 10 to 15 minutes. The flask should be covered with a watch glass during boiling in order to prevent oxidation of the iron. Filter rapidly and wash the precipitate twice with hot water. Transfer the filter paper and contents to a platinum crucible and ignite it. Fuse the residue with a mixture of 5 g. of sodium carbonate and not more than 0.25 g. of potassium nitrate. The use of an excessive amount of potassium nitrate will bring about the solution of platinum from the crucible which may give the solution a yellow color. Dissolve the fusion in 50 ml. of water, transfer it to a beaker, and add 2 ml. of 3% hydrogen peroxide to reduce any permanganate ion present. Boil the solution for a few minutes to decompose excess hydrogen peroxide and filter. Dilute the solution to 200 ml. and reserve it for comparison with a standard solution of sodium chromate.

Standard Chromate Solution. — Prepare a standard chromate solution by dissolving 6.580 g. of $Na_2CrO_4 \cdot 10H_2O$ in distilled water. Make the solution alkaline with 1 g. of sodium carbonate and dilute to one liter. Each milliliter of this solution is equivalent to 1 mg. of chromium. This solution may be further diluted if required to produce a solution containing 0.1 mg. or 0.01 mg. of chromium per milliliter.

Comparison of Unknown and Standard Solutions. — Following the instructions given in §§ 532 and 533, compare the unknown

[20] This method is adapted from Snell, "Colorimetric Methods of Analysis." See § 11.

and standard solutions. From the results of this comparison calculate the concentration of chromate in the unknown. From the concentration of chromate, the volume of the unknown solution and the weight of the sample taken for analysis, calculate the per cent of Cr in the sample of steel.

535. Gradation Photometers. Visual Matching. — The principle upon which gradation photometers are based is essentially as follows (see Figure 129): Light from a suitable source, usually a filament lamp, is divided by means of lenses into two parallel,
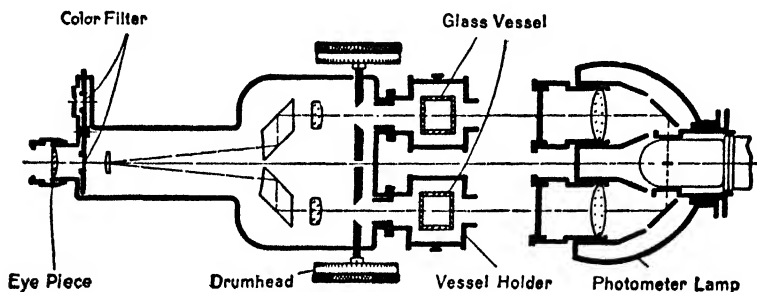
Fig. 129

Optical Diagram of the Pulfrich Photometer

closely adjacent beams of equal intensity. One beam is passed in successive order through a glass cell containing the solution under examination, a small variable square aperture the size of which can be regulated precisely,[21] a condenser lens, a totally reflecting prism, a biprism, an appropriate color filter,[22] and an eyepiece, so that the beam appears to the observer as one-half of the field of view. The other beam follows a similar course except that it passes through a glass cell containing only the solvent. The opening of the variable aperture for each beam is regulated by

[21] Other devices which are employed in place of a variable aperture for regulating the intensity of a light beam are a compensating wedge and a polarizing equipment.

[22] It is to be remembered that color filters do not isolate light of substantially a single wave length, but light of a main spectral line accompanied by neighboring lines of shorter and of longer wave lengths, depending on the nature of the filter as well as on its thickness.

means of its own screw device attached to a calibrated drum; at maximum openings the sizes of the two apertures are equal, and the drums are so calibrated that the readings are proportional to the amounts of light passing through the respective apertures. The ratio of the intensity of the comparison beam with aperture diminished to give equal half fields of view with respect to the beam passing through the sample, to the intensity of the comparison beam with aperture wide open, is the transmission factor. In very exact work a correction must be made for reflection losses.

The transmission factor E is determined with a given filter for both a known solution and the unknown solution. From the values of these transmission factors the corresponding extinction coefficients are calculated, as explained in §§ 515 and 516. In cases in which Beer's law holds, we have

$$\frac{K_S}{K_U} = \frac{C_S}{C_U}$$

where K_S and K_U are the extinction coefficients of the known and unknown solutions respectively, and where C_S and C_U are the concentrations of these solutions.

In cases where Beer's law does not hold, we have

$$\frac{K_S}{K_U} = \frac{\phi_S C_S}{\phi_U C_S}$$

where ϕ_S and ϕ_U are variables for the known and unknown solutions respectively.

536. Gradation Photometers. Photoelectric Matching. — The optical arrangement of gradation photometers when used for photoelectric matching is the same as that described in the preceding paragraph, but the matching of the intensities of the two beams is made by means of photoelectric cells in place of the eye. As pithily stated by R. H. Müller in a recent article,[23] "the substitution of photocells for the eye has been accomplished in a number of ways. . . . Measurements have been reported which exceed in precision and reliability the values which can be obtained with the very best visual instruments. These results are invariably

[23] Photoelectric Methods in Analytical Chemistry. *Ind. Eng. Chem., Anal. Ed.* **11**, 1 (1939).

obtained with instruments which embody sound optical theory and practice and the best resources of electrical measurements. They are usually photoelectric spectrophotometers, and are necessarily elaborate and expensive. Simple compromise instruments have been described in great number and are justified by reasons of expediency, elimination of fatigue, or greater speed of operation. They rarely justify exaggerated claims of superiority over existing visula instruments. . . . In general it may be said that the adaptation of photocells to existing visual instruments is poor practice and wholly inadvisable."

537. Photoelectric Cells. Types and References. — In his article Professor Muller proceeds in detailed fashion to consider the various methods of using photoelectric cells, namely, single cell methods, flicker methods, two-cell methods; he discusses the characteristics of the two types of photoelectric cells that are used, namely, the high-vacuum cell and the barrier-layer type; he also considers light sources and their adaptation; monochromators and filters, and types of circuits and their utility. At the end of his article he gives an extended list of 24 monographs and 239 references, all of which will be found invaluable to those wishing to study this field further.

538. Spectrophotometer. — The spectrophotometer is the most elaborate and reliable instrument for photometric investigations; its general principle is that described in § 509 but, owing to the complexity of the optical arrangements, a consideration of which is beyond the scope of this work, the reader is referred to the authoritative manual by F. Twyman and C. B. Allsop, "The Practice of Absorption Spectrophotometry with Hilger Instruments," 2nd ed., Adam Hilger, Ltd.   London, 1934.

539. Transmission Factors of Optically Heterogeneous Materials. — The problem of measuring the transmitted light in cases involving optically heterogeneous materials is much more complex than in the case of homogeneous materials; moreover, Bouguer's (Lambert's) Law does not apply unless the particles of the disperse phase are uniformly very small and the depth of column is not too great.   In view of the complexity of the case, the authors feel that any adequate treatment is beyond their immediate purpose, and the student is referred to: P. V. Wells, "Present

Status of Turbidity Measurements," *Chem. Rev.*, **3**, 331 (1927).
Chamon, F. F. Renwick and B. V. Storr, *Photogr. J.*, **58**, 121 (1918).
J. H. Yoe, "Photometric Chemical Analysis," Vol. II, Nephelome-
try.   John Wiley & Sons, Inc., New York, 1939.

540. Examples.

1. Calculate the energy radiated by a black body in the interval 679.5–680.5mμ, for the temperatures 2000° K, 3000° K, 4000° K and 6000° K. Compare with the values shown in Figure 117.

2. Calculate the transmission factors for depths of 1, 2, 3, 4 cm. and values of the extinction coefficient equal to 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and plot the results to appropriate scale.

3. Calculate the optical density of the sample of glass mentioned in § 512 for wave lengths of 460 mμ, 590 mμ and 680 mμ for the thickness 0.1, 0.2, 0.4, and 0.8 cm.

4. Show that if we have only two solutes in a solution and know the extinction coefficient of each solute for various wave lengths, and if Beer's Law applies to each solute, then we can calculate the percentage of each solute from the transmission factors of the solution for the designated wave lengths.

5. In the determination of haemoglobin in the blood, it is found, when light of wave length 572 mμ is used, and 25 cu. mm. of blood is diluted to 2500 cu. mm. with alcohol and this diluted solution is examined through a stratum thickness of 5 mm. with light of wave length 578 mμ, that an extinction coefficient of 1.00 corresponds to a concentration of 33.0 g. haemoglobin per 100 ml. of blood.   In the examination of a sample of patient's blood by the above method, an extinction coefficient of 0.46 was obtained.   What was the haemoglobin content?

<div align="right">Ans.   15.2 g. per 100 ml. of blood.</div>

APPENDIX

CONTENTS

541.   LOGARITHMS OF NUMBERS[1]

N.	0	1	2	3	4	5	6	7	8	9
100	00 000	043	087	130	173	217	260	303	346	389
101	432	475	518	561	604	647	689	732	775	817
102	860	903	945	988	*030	*072	*115	*157	*199	*242
103	01 284	326	368	410	452	494	536	578	620	662
104	703	745	787	828	870	912	953	995	*036	*078
105	02 119	160	202	243	284	325	366	407	449	490
106	531	572	612	653	694	735	776	816	857	898
107	938	979	*019	*060	*100	*141	*181	*222	*262	*302
108	03 342	383	423	463	503	543	583	623	663	703
109	743	782	822	862	902	941	981	*021	*060	*100
110	04 139	179	218	258	297	336	376	415	454	493
111	532	571	610	650	689	727	766	805	844	883
112	922	961	999	*038	*077	*115	*154	*192	*231	*269
113	05 308	346	385	423	461	500	538	576	614	652
114	690	729	767	805	843	881	918	956	994	*032
115	06 070	108	145	183	221	258	296	333	371	408
116	446	483	521	558	595	633	670	707	744	781
117	819	856	893	930	967	*004	*041	*078	*115	*151
118	07 188	225	262	298	335	372	408	445	482	518
119	555	591	628	664	700	737	773	809	846	882
120	918	954	990	*027	*063	*099	*135	*171	*207	*243
121	08 279	314	350	386	422	458	493	529	565	600
122	636	672	707	743	778	814	849	884	920	955
123	991	*026	*061	*096	*132	*167	*202	*237	*272	*307
124	09 342	377	412	447	482	517	552	587	621	656
125	691	726	760	795	830	864	899	934	968	*003
126	10 037	072	106	140	175	209	243	278	312	346
127	380	415	449	483	517	551	585	619	653	687
128	721	755	789	823	857	890	924	958	992	*025
129	11 059	093	126	160	193	227	261	294	327	361
130	394	428	461	494	528	561	594	628	661	694
131	727	760	793	826	860	893	926	959	992	*024
132	12 057	090	123	156	189	222	254	287	320	352
133	385	418	450	483	516	548	581	613	646	678
134	710	743	775	808	840	872	905	937	969	*001
135	13 033	066	098	130	162	194	226	258	290	322
136	354	386	418	450	481	513	545	577	609	640
137	672	704	735	767	799	830	862	893	925	956
138	988	*019	*051	*082	*114	*145	*176	*208	*239	*270
139	14 301	333	364	395	426	457	489	520	551	582
140	613	644	675	706	737	768	799	829	860	891
141	922	953	983	*014	*045	*076	*106	*137	*168	*198
142	15 229	259	290	320	351	381	412	442	473	503
143	534	564	594	625	655	685	715	746	776	806
144	836	866	897	927	957	987	*017	*047	*077	*107
145	16 137	167	197	227	256	286	316	346	376	406
146	435	465	495	524	554	584	613	643	673	702
147	732	761	791	820	850	879	909	938	967	997
148	17 026	056	085	114	143	173	202	231	260	289
149	319	348	377	406	435	464	493	522	551	580

P. P.

	44	43	42
1	4	4	4
2	9	9	8
3	13	13	13
4	18	17	17
5	22	22	21
6	26	26	25
7	31	30	29
8	35	34	34
9	40	39	38

	41	40	39
1	4	4	4
2	8	8	8
3	12	12	12
4	16	16	16
5	21	20	20
6	25	24	23
7	29	28	27
8	33	32	31
9	37	36	35

	38	37	36
1	4	4	4
2	8	7	7
3	11	11	11
4	15	15	14
5	19	19	18
6	23	22	22
7	27	26	25
8	30	30	29
9	34	33	32

	35	34	33
1	4	3	3
2	7	7	7
3	11	10	10
4	14	14	13
5	18	17	17
6	21	20	20
7	25	24	23
8	28	27	26
9	32	31	30

	32	31	30
1	3	3	3
2	6	6	6
3	10	9	9
4	13	12	12
5	16	16	15
6	19	19	18
7	22	22	21
8	26	25	24
9	29	28	27

N.	0	1	2	3	4	5	6	7	8	9

P. P.

[1] This table has been verified by comparison with the values given in the following publication, "A New Manual of Logarithms to Seven Places," edited by Dr. C. Bruhns, 11th stereotype edition, Bernhard Tauchnitz, Leipzig, 1913; Lemcke & Buechner, New York, 1913.

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9
150	17 609	638	667	696	725	754	782	811	840	869
151	898	926	955	984	*013	*041	*070	*099	*127	*156
152	18 184	213	241	270	298	327	355	384	412	441
153	469	498	526	554	583	611	639	667	696	724
154	752	780	808	837	865	893	921	949	977	*005
155	19 033	061	089	117	145	173	201	229	257	285
156	312	340	368	396	424	451	479	507	535	562
157	590	618	645	673	700	728	756	783	811	838
158	866	893	921	948	976	*003	*030	*058	*085	*112
159	20 140	167	194	222	249	276	303	330	358	385
160	412	439	466	493	520	548	575	602	629	656
161	683	710	737	763	790	817	844	871	898	925
162	952	978	*005	*032	*059	*085	*112	*139	*165	*192
163	21 219	245	272	299	325	352	378	405	431	458
164	484	511	537	564	590	617	643	669	696	722
165	748	775	801	827	854	880	906	932	958	985
166	22 011	037	063	089	115	141	167	194	220	246
167	272	298	324	350	376	401	427	453	479	505
168	531	557	583	608	634	660	686	712	737	763
169	789	814	840	866	891	917	943	968	994	*019
170	23 045	070	096	121	147	172	198	223	249	274
171	300	325	350	376	401	426	452	477	502	528
172	553	578	603	629	654	679	704	729	754	779
173	805	830	855	880	905	930	955	980	*005	*030
174	24 055	080	105	130	155	180	204	229	254	279
175	304	329	353	378	403	428	452	477	502	527
176	551	576	601	625	650	674	699	724	748	773
177	797	822	846	871	895	920	944	969	993	*018
178	25 042	066	091	115	139	164	188	212	237	261
179	285	310	334	358	382	406	431	455	479	503
180	527	551	575	600	624	648	672	696	720	744
181	768	792	816	840	864	888	912	935	959	983
182	26 007	031	055	079	102	126	150	174	198	221
183	245	269	293	316	340	364	387	411	435	458
184	482	505	529	553	576	600	623	647	670	694
185	717	741	764	788	811	834	858	881	905	928
186	951	975	998	*021	*045	*068	*091	*114	*138	*161
187	27 184	207	231	254	277	300	323	346	370	393
188	416	439	462	485	508	531	554	577	600	623
189	646	669	692	715	738	761	784	807	830	852
190	875	898	921	944	967	989	*012	*035	*058	*081
191	28 103	126	149	171	194	217	240	262	285	307
192	330	353	375	398	421	443	466	488	511	533
193	556	578	601	623	646	668	691	713	735	758
194	780	803	825	847	870	892	914	937	959	981
195	29 003	026	048	070	092	115	137	159	181	203
196	226	248	270	292	314	336	358	380	403	425
197	447	469	491	513	535	557	579	601	623	645
198	667	688	710	732	754	776	798	820	842	863
199	885	907	929	951	973	994	*016	*038	*060	*081
N.	0	1	2	3	4	5	6	7	8	9

P. P.

	29	28
1	3	3
2	6	6
3	9	8
4	12	11
5	15	14
6	17	17
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8	23	22
9	26	25

	27	26
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2	5	5
3	8	8
4	11	10
5	14	13
6	16	16
7	19	18
8	22	21
9	24	23

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	24	23
1	2	2
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3	7	7
4	10	9
5	12	12
6	14	14
7	17	16
8	19	18
9	22	21

	22	21
1	2	2
2	4	4
3	7	6
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5	11	11
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7	15	15
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Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9
200	30 103	125	146	168	190	211	233	255	276	298
201	320	341	363	384	406	428	449	471	492	514
202	535	557	578	600	621	643	664	685	707	728
203	750	771	792	814	835	856	878	899	920	942
204	963	984	*006	*027	*048	*069	*091	*112	*133	*154
205	31 175	197	218	239	260	281	302	323	345	366
206	387	408	429	450	471	492	513	534	555	576
207	597	618	639	660	681	702	723	744	765	785
208	806	827	848	869	890	911	931	952	973	994
209	32 015	035	056	077	098	118	139	160	181	201
210	222	243	263	284	305	325	346	366	387	408
211	428	449	469	490	510	531	552	572	593	613
212	634	654	675	695	715	736	756	777	797	818
213	838	858	879	899	919	940	960	980	*001	*021
214	33 041	062	082	102	122	143	163	183	203	224
215	244	264	284	304	325	345	365	385	405	425
216	445	465	486	506	526	546	566	586	606	626
217	646	666	686	706	726	746	766	786	806	826
218	846	866	885	905	925	945	965	985	*005	*025
219	34 044	064	084	104	124	143	163	183	203	223
220	242	262	282	301	321	341	361	380	400	420
221	439	459	479	498	518	537	557	577	596	616
222	635	655	674	694	713	733	753	772	792	811
223	830	850	869	889	908	928	947	967	986	*005
224	35 025	044	064	083	102	122	141	160	180	199
225	218	238	257	276	295	315	334	353	372	392
226	411	430	449	468	488	507	526	545	564	583
227	603	622	641	660	679	698	717	736	755	774
228	793	813	832	851	870	889	908	927	946	965
229	984	*003	*021	*040	*059	*078	*097	*116	*135	*154
230	36 173	192	211	229	248	267	286	305	324	342
231	361	380	399	418	436	455	474	493	511	530
232	549	568	586	605	624	642	661	680	698	717
233	736	754	773	791	810	829	847	866	884	903
234	922	940	959	977	996	*014	*033	*051	*070	*088
235	37 107	125	144	162	181	199	218	236	254	273
236	291	310	328	346	365	383	401	420	438	457
237	475	493	511	530	548	566	585	603	621	639
238	658	676	694	712	731	749	767	785	803	822
239	840	858	876	894	912	931	949	967	985	*003
240	38 021	039	057	075	093	112	130	148	166	184
241	202	220	238	256	274	292	310	328	346	364
242	382	399	417	435	453	471	489	507	525	543
243	561	578	596	614	632	650	668	686	703	721
244	739	757	775	792	810	828	846	863	881	899
245	917	934	952	970	987	*005	*023	*041	*058	*076
246	39 094	111	129	146	164	182	199	217	235	252
247	270	287	305	322	340	358	375	393	410	428
248	445	463	480	498	515	533	550	568	585	602
249	620	637	655	672	690	707	724	742	759	777
N.	0	1	2	3	4	5	6	7	8	9

P. P.

	22	21
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7	15	15
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LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9
250	39 794	811	829	846	863	881	898	915	933	950
251	967	985	*002	*019	*037	*054	*071	*088	*106	*123
252	40 140	157	175	192	209	226	243	261	278	295
253	312	329	346	364	381	398	415	432	449	466
254	483	500	518	535	552	569	586	603	620	637
255	654	671	688	705	722	739	756	773	790	807
256	824	841	858	875	892	909	926	943	960	976
257	993	*010	*027	*044	*061	*078	*095	*111	*128	*145
258	41 162	179	196	212	229	246	263	280	296	313
259	330	347	363	380	397	414	430	447	464	481
260	497	514	531	547	564	581	597	614	631	647
261	664	681	697	714	731	747	764	780	797	814
262	830	847	863	880	896	913	929	946	963	979
263	996	*012	*029	*045	*062	*078	*095	*111	*127	*144
264	42 160	177	193	210	226	243	259	275	292	308
265	325	341	357	374	390	406	423	439	455	472
266	488	504	521	537	553	570	586	602	619	635
267	651	667	684	700	716	732	749	765	781	797
268	813	830	846	862	878	894	911	927	943	959
269	975	991	*008	*024	*040	*056	*072	*088	*104	*120
270	43 136	152	169	185	201	217	233	249	265	281
271	297	313	329	345	361	377	393	409	425	441
272	457	473	489	505	521	537	553	569	584	600
273	616	632	648	664	686	696	712	727	743	759
274	775	791	807	823	838	854	870	886	902	917
275	933	949	965	981	996	*012	*028	*044	*059	*075
276	44 091	107	122	138	154	170	185	201	217	232
277	248	264	279	295	311	326	342	358	373	389
278	404	420	436	451	467	483	498	514	529	545
279	560	576	592	607	623	638	654	669	685	700
280	716	731	747	762	778	793	809	824	840	855
281	871	886	902	917	932	948	963	979	994	*010
282	45 025	040	056	071	086	102	117	133	148	163
283	179	194	209	225	240	255	271	286	301	317
284	332	347	362	378	393	408	423	439	454	469
285	484	500	515	530	545	561	576	591	606	621
286	637	652	667	682	697	712	728	743	758	773
287	788	803	818	834	849	864	879	894	909	924
288	939	954	969	984	*000	*015	*030	*045	*060	*075
289	46 090	105	120	135	150	165	180	195	210	225
290	210	255	270	285	300	315	330	345	359	374
291	389	404	419	434	449	464	479	494	509	523
292	538	553	568	583	598	613	627	642	657	672
293	687	702	716	731	746	761	776	790	805	820
294	835	850	864	879	894	909	923	938	953	967
295	982	997	*012	*026	*041	*056	*070	*085	*100	*114
296	47 129	144	159	173	188	202	217	232	246	261
297	276	290	305	319	334	349	363	378	392	407
298	422	436	451	465	480	494	509	524	538	553
299	567	582	596	611	625	640	654	669	683	698
N.	0	1	2	3	4	5	6	7	8	9

P. P.

	18		17		16		15		14
1	2	1	2	1	2	1	2	1	1
2	4	2	3	2	3	2	3	2	3
3	5	3	5	3	5	3	5	3	4
4	7	4	7	4	6	4	6	4	6
5	9	5	9	5	8	5	8	5	7
6	11	6	10	6	10	6	9	6	8
7	13	7	12	7	11	7	11	7	10
8	14	8	14	8	13	8	12	8	11
9	16	9	15	9	14	9	14	9	13

Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9
300	47 712	727	741	756	770	784	799	813	828	842
301	857	871	885	900	914	929	943	958	972	986
302	48 001	015	029	044	058	073	087	101	116	130
303	144	159	173	187	202	216	230	244	259	273
304	287	302	316	330	344	359	373	387	401	416
305	430	444	458	473	487	501	515	530	544	558
306	572	586	601	615	629	643	657	671	686	700
307	714	728	742	756	770	785	799	813	827	841
308	855	869	883	897	911	926	940	954	968	982
309	996	*010	*024	*038	*052	*066	*080	*094	*108	*122
310	49 136	150	164	178	192	206	220	234	248	262
311	276	290	304	318	332	346	360	374	388	402
312	415	429	443	457	471	485	499	513	527	541
313	554	568	582	596	610	624	638	651	665	679
314	693	707	721	734	748	762	776	790	803	817
315	831	845	859	872	886	900	914	927	941	955
316	969	982	996	*010	*024	*037	*051	*065	*079	*092
317	50 106	120	133	147	161	174	188	202	215	229
318	243	256	270	284	297	311	325	338	352	365
319	379	393	406	420	433	447	461	474	488	501
320	515	529	542	556	569	583	596	610	623	637
321	651	664	678	691	705	718	732	745	759	772
322	786	799	813	826	839	853	866	880	893	907
323	920	934	947	961	974	987	*001	*014	*028	*041
324	51 055	068	081	095	108	121	135	148	162	175
325	188	202	215	228	242	255	268	282	295	308
326	322	335	348	362	375	388	402	415	428	441
327	455	468	481	495	508	521	534	548	561	574
328	587	601	614	627	640	654	667	680	693	706
329	720	733	746	759	772	786	799	812	825	838
330	851	865	878	891	904	917	930	943	957	970
331	983	996	*009	*022	*035	*048	*061	*075	*088	*101
332	52 114	127	140	153	166	179	192	205	218	231
333	244	257	270	284	297	310	323	336	349	362
334	375	388	401	414	427	440	453	466	479	492
335	504	517	530	543	556	569	582	595	608	621
336	634	647	660	673	686	699	711	724	737	750
337	763	776	789	802	815	827	840	853	866	879
338	892	905	917	930	943	956	969	982	994	*007
339	53 020	033	046	058	071	084	097	110	122	135
340	148	161	173	186	199	212	224	237	250	263
341	275	288	301	314	326	339	352	364	377	390
342	403	415	428	441	453	466	479	491	504	517
343	529	542	555	567	580	593	605	618	631	643
344	656	668	681	694	706	719	732	744	757	769
345	782	794	807	820	832	845	857	870	882	895
346	908	920	933	945	958	970	983	995	*008	*020
347	54 033	045	058	070	083	095	108	120	133	145
348	158	170	183	195	208	220	233	245	258	270
349	283	295	307	320	332	345	357	370	382	394

P. P.

	15		14		13		12
1	2	1	1	1	1	1	1
2	3	2	3	2	3	2	2
3	5	3	4	3	4	3	4
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5	8	5	7	5	7	5	6
6	9	6	8	6	8	6	7
7	11	7	10	7	9	7	8
8	12	8	11	8	10	8	10
9	14	9	13	9	12	9	11

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
350	54 407	419	432	444	456	469	481	494	506	518		
351	531	543	555	568	580	593	605	617	630	642		**13**
352	654	667	679	691	704	716	728	741	753	765	1	1
353	777	790	802	814	827	839	851	864	876	888	2	3
354	900	913	925	937	949	962	974	986	998	*011	3	4
											4	5
355	55 023	035	047	060	072	084	096	108	121	123	5	7
356	145	157	169	182	194	206	218	230	242	255	6	8
357	267	279	291	303	315	328	340	352	364	376	7	9
358	388	400	413	425	437	449	461	473	485	497	8	10
359	509	522	534	546	558	570	582	594	606	618	9	12
360	630	642	654	666	678	691	703	715	727	739		
361	751	763	775	787	799	811	823	835	847	859		
362	871	883	895	907	919	931	943	955	967	979		
363	991	*003	*015	*027	*038	*050	*062	*074	*086	*098		
364	56 110	122	134	146	158	170	182	194	205	217		
												12
365	229	241	253	265	277	289	301	312	324	336	1	1
366	348	360	372	384	396	407	419	431	443	455	2	2
367	467	478	490	502	514	526	538	549	561	573	3	4
368	585	597	608	620	632	644	656	667	679	691	4	5
369	703	714	726	738	750	761	773	785	797	808	5	6
											6	7
370	820	832	844	855	867	879	891	902	914	926	7	8
371	937	949	961	972	984	996	*008	*019	*031	*043	8	10
372	57 054	066	078	089	101	113	124	136	148	159	9	11
373	171	183	194	206	217	229	241	252	264	276		
374	287	299	310	322	334	345	357	368	380	392		
375	403	415	426	438	449	461	473	484	496	507		
376	519	530	542	553	565	576	588	600	611	623		
377	634	646	657	669	680	692	703	715	726	738		
378	749	761	772	784	795	807	818	830	841	852		**11**
379	864	875	887	898	910	921	933	944	955	967	1	1
											2	2
380	978	990	*001	*013	*024	*035	*047	*058	*070	*081	3	3
381	58 092	104	115	127	138	149	161	172	184	195	4	4
382	206	218	229	240	252	263	274	286	297	309	5	6
383	320	331	343	354	365	377	388	399	410	422	6	7
384	433	444	456	467	478	490	501	512	524	535	7	8
											8	9
385	546	557	569	580	591	602	614	625	636	647	9	10
386	659	670	681	692	704	715	726	737	749	760		
387	771	782	794	805	816	827	838	850	861	872		
388	883	894	906	917	928	939	950	961	973	984		
389	995	*006	*017	*028	*040	*051	*062	*073	*084	*095		
390	59 106	118	129	140	151	162	173	184	195	207		
391	218	229	240	251	262	273	284	295	306	318		**10**
392	329	340	351	362	373	384	395	406	417	428	1	1
393	439	450	461	472	483	494	506	517	528	539	2	2
394	550	561	572	583	594	605	616	627	638	649	3	3
											4	4
395	660	671	682	693	704	715	726	737	748	759	5	5
396	770	780	791	802	813	824	835	846	857	868	6	6
397	879	890	901	912	923	934	945	956	966	977	7	7
398	988	999	*010	*021	*032	*043	*054	*065	*076	*086	8	8
399	60 097	108	119	130	141	152	163	173	184	195	9	9
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
400	60 206	217	228	239	249	260	271	282	293	304		
401	314	325	336	347	358	369	379	390	401	412		
402	423	433	444	455	466	477	487	498	509	520		
403	531	541	552	563	574	584	595	606	617	627		
404	638	649	660	670	681	692	703	713	724	735		
405	746	756	767	778	788	799	810	821	831	842		
406	853	863	874	885	895	906	917	927	938	949		**11**
407	959	970	981	991	*002	*013	*023	*034	*045	*055	1	1
408	61 066	077	087	098	109	119	130	140	151	162	2	2
409	172	183	194	204	215	225	236	247	257	268	3	3
											4	4
410	278	289	300	310	321	331	342	352	363	374	5	6
411	384	395	405	416	426	437	418	458	469	479	6	7
412	490	500	511	521	532	542	553	563	574	584	7	8
413	595	606	616	627	637	648	658	669	679	690	8	9
414	700	711	721	731	742	752	763	773	784	794	9	10
415	805	815	826	836	847	857	868	878	888	899		
416	909	920	930	941	951	962	972	982	993	*003		
417	62 014	024	034	045	055	066	076	086	097	107		
418	118	128	138	149	159	170	180	190	201	211		
419	221	232	242	252	263	273	284	294	304	315		
420	325	335	346	356	366	377	387	397	408	418		
421	428	439	449	459	469	480	490	500	511	521		**10**
422	531	542	552	562	572	583	593	603	613	624	1	1
423	634	644	655	665	675	685	696	706	716	726	2	2
424	737	747	757	767	778	788	798	808	818	829	3	3
											4	4
425	839	849	859	870	880	890	900	910	921	931	5	5
426	941	951	961	972	982	992	*002	*012	*022	*033	6	6
427	63 043	053	063	073	083	094	104	114	124	134	7	7
428	144	155	165	175	185	195	205	215	225	236	8	8
429	246	256	266	276	286	296	306	317	327	337	9	9
430	347	357	367	377	387	397	407	417	428	438		
431	448	458	468	478	488	498	508	518	528	538		
432	548	558	568	579	589	599	609	619	629	639		
433	649	659	669	679	689	699	709	719	729	739		
434	749	759	769	779	789	799	809	819	829	839		
435	849	859	869	879	889	899	909	919	929	939		
436	949	959	969	979	988	998	*008	*018	*028	*038		**9**
437	64 048	058	068	078	088	098	108	118	128	137	1	1
438	147	157	167	177	187	197	207	217	227	237	2	2
439	246	256	266	276	286	296	306	316	326	335	3	3
											4	4
440	345	355	365	375	385	395	404	414	424	434	5	5
441	444	454	464	473	483	493	503	513	523	532	6	5
442	542	552	562	572	582	591	601	611	621	631	7	6
443	640	650	660	670	680	689	699	709	719	729	8	7
444	738	748	758	768	777	787	797	807	816	826	9	8
445	836	846	856	865	875	885	895	904	914	924		
446	933	943	953	963	972	982	992	*002	*011	*021		
447	65 031	040	050	060	070	079	089	099	108	118		
448	128	137	147	157	167	176	186	196	205	215		
449	225	234	244	254	263	273	283	292	302	312		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
450	65 321	331	341	350	360	369	379	389	398	408		
451	418	427	437	447	456	466	475	485	495	504		
452	514	523	533	543	552	562	571	581	591	600		
453	610	619	629	639	648	658	667	677	686	696		
454	706	715	725	734	744	753	763	772	782	792		
455	801	811	820	830	839	849	858	868	877	887		
456	896	906	916	925	935	944	954	963	973	982		**10**
457	992	*001	*011	*020	*030	*039	*049	*058	*068	*077	1	1
458	66 087	096	106	115	124	134	143	153	162	172	2	2
459	181	191	200	210	219	229	238	247	257	266	3	3
											4	4
460	276	285	295	304	314	323	332	342	351	361	5	5
461	370	380	389	398	408	417	427	436	445	455	6	6
462	464	474	483	492	502	511	521	530	539	549	7	7
463	558	567	577	586	596	605	614	624	633	642	8	8
464	652	661	671	680	689	699	708	717	727	736	9	9
465	745	755	764	773	783	792	801	811	820	829		
466	839	848	857	867	876	885	894	904	913	922		
467	932	941	950	960	969	978	957	997	*006	*015		
468	67 025	034	043	052	062	071	080	089	099	108		
469	117	127	136	145	154	164	173	182	191	201		
470	210	219	228	237	247	256	265	274	284	293		
471	302	311	321	330	339	348	357	367	376	385		**9**
472	394	403	413	422	431	440	449	459	468	477	1	1
473	486	495	504	514	523	532	541	550	560	569	2	2
474	578	587	596	605	614	624	633	642	651	660	3	3
											4	4
475	669	679	688	697	706	715	724	733	742	752	5	5
476	761	770	779	788	797	806	815	825	834	843	6	5
477	852	861	870	879	888	897	906	916	925	934	7	6
478	943	952	961	970	979	988	997	*006	*015	*024	8	7
479	68 034	043	052	061	070	079	088	097	106	115	9	8
480	124	133	142	151	160	169	178	187	196	205		
481	215	224	233	242	251	260	269	278	287	296		
482	305	314	323	332	341	350	359	368	377	386		
483	395	404	413	422	431	440	449	458	467	476		
484	485	494	502	511	520	529	538	547	556	565		
485	574	583	592	601	610	619	628	637	646	655		
486	664	673	681	690	699	708	717	726	735	744		**8**
487	753	762	771	780	789	797	806	815	824	833	1	1
488	842	851	860	869	878	886	895	904	913	922	2	2
489	931	940	949	958	966	975	984	993	*002	*011	3	2
											4	3
490	69 020	028	037	046	055	064	073	082	090	099	5	4
491	108	117	126	135	144	152	161	170	179	188	6	5
492	197	205	214	223	232	241	249	258	267	276	7	6
493	285	294	302	311	320	329	338	346	355	364	8	6
494	373	381	390	399	408	417	425	434	443	452	9	7
495	461	469	478	487	496	504	513	522	531	539		
496	548	557	566	574	583	592	601	609	618	627		
497	636	644	653	662	671	679	688	697	705	714		
498	723	732	740	749	758	767	775	784	793	801		
499	810	819	827	836	845	854	862	871	880	888		
N.	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**P. P.**	

Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9
500	69 897	906	914	923	932	940	949	958	966	975
501	984	992	*001	*010	*018	*027	*036	*044	*053	*062
502	70 070	079	088	096	105	114	122	131	140	148
503	157	165	174	183	191	200	209	217	226	234
504	243	252	260	269	278	286	295	303	312	321
505	329	338	346	355	364	372	381	389	398	406
506	415	424	432	441	449	458	467	475	484	492
507	501	509	518	526	535	544	552	561	569	578
508	586	595	603	612	621	629	638	646	655	663
509	672	680	689	697	706	714	723	731	740	749
510	757	766	774	783	791	800	808	817	825	834
511	842	851	859	868	876	885	893	902	910	919
512	927	935	944	952	961	969	978	986	995	*003
513	71 012	020	029	037	046	054	063	071	079	088
514	096	105	113	122	130	139	147	155	164	172
515	181	189	198	206	214	223	231	240	248	257
516	265	273	282	290	299	307	315	324	332	341
517	349	357	366	374	383	391	399	408	416	425
518	433	441	450	458	466	475	483	492	500	508
519	517	525	533	542	550	559	567	575	584	592
520	600	609	617	625	634	642	650	659	667	675
521	684	692	700	709	717	725	734	742	750	759
522	767	775	784	792	800	809	817	825	834	842
523	850	858	867	875	883	892	900	908	917	925
524	933	941	950	958	966	975	983	991	999	*008
525	72 016	024	032	041	049	057	066	074	082	090
526	099	107	115	123	132	140	148	156	165	173
527	181	189	198	206	214	222	230	239	247	255
528	263	272	280	288	296	304	313	321	329	337
529	346	354	362	370	378	387	395	403	411	419
530	428	436	444	452	460	469	477	485	493	501
531	509	518	526	534	542	550	558	567	575	583
532	591	599	607	616	624	632	640	648	656	665
533	673	681	689	697	705	713	722	730	738	746
534	754	762	770	779	787	795	803	811	819	827
535	835	843	852	860	868	876	884	892	900	908
536	916	925	933	941	949	957	965	973	981	989
537	997	*006	*014	*022	*030	*038	*046	*054	*062	*070
538	73 078	086	094	102	111	119	127	135	143	151
539	159	167	175	183	191	199	207	215	223	231
540	239	247	255	263	272	280	288	296	304	312
541	320	328	336	344	352	360	368	376	384	392
542	400	408	416	424	432	440	448	456	464	472
543	480	488	496	504	512	520	528	536	544	552
544	560	568	576	584	592	600	608	616	624	632
545	640	648	656	664	672	679	687	695	703	711
546	719	727	735	743	751	759	767	775	783	791
547	799	807	815	823	830	838	846	854	862	870
548	878	886	894	902	910	918	926	933	941	949
549	957	965	973	981	989	997	*005	*013	*020	*028

P. P.

9		8		7	
1	1	1	1	1	1
2	2	2	2	2	1
3	3	3	2	3	2
4	4	4	3	4	3
5	5	5	4	5	4
6	5	6	5	6	4
7	6	7	6	7	5
8	7	8	6	8	6
9	8	9	7	9	6

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
550	74 036	044	052	060	068	076	084	092	099	107		
551	115	123	131	139	147	155	162	170	178	186		
552	194	202	210	218	225	233	241	249	257	265		
553	273	280	288	296	304	312	320	327	335	343		
554	351	359	367	374	382	390	398	406	414	421		
555	429	437	445	453	461	468	476	484	492	500		
556	507	515	523	531	539	547	554	562	570	578		
557	586	593	601	609	617	624	632	640	648	656		
558	663	671	679	687	695	702	710	718	726	733		
559	741	749	757	764	772	780	788	796	803	811		
560	819	827	834	842	850	858	865	873	881	889		
561	896	904	912	920	927	935	943	950	958	966		8
562	974	981	989	997	*005	*012	*020	*028	*035	*043	1	1
563	75 051	059	066	074	082	089	097	105	113	120	2	2
564	128	136	143	151	159	166	174	182	189	197	3	2
											4	3
565	205	213	220	228	236	243	251	259	266	274	5	4
566	282	289	297	305	312	320	328	335	343	351	6	5
567	358	366	374	381	389	397	404	412	420	427	7	(
568	435	442	450	458	465	473	481	488	496	504	8	6
569	511	519	526	534	542	549	557	565	572	580	9	7
570	587	595	603	610	618	626	633	641	648	656		
571	664	671	679	686	694	702	709	717	724	732		
572	740	747	755	762	770	778	785	793	800	808		
573	815	823	831	838	846	853	861	868	876	884		
574	891	899	906	914	921	929	937	944	952	959		
575	967	974	982	989	997	*005	*012	*020	*027	*035		
576	76 042	050	057	065	072	080	087	095	103	110		
577	118	125	133	140	148	155	163	170	178	185		
578	193	200	208	215	223	230	238	245	253	260		
579	268	275	283	290	298	305	313	320	328	335		
580	343	350	358	365	373	380	388	395	403	410		
581	418	425	433	440	448	455	462	470	477	485		7
582	492	500	507	515	522	530	537	545	552	559	1	1
583	567	574	582	589	597	604	612	619	626	634	2	1
584	641	649	656	664	671	678	686	693	701	708	3	2
											4	3
585	716	723	730	738	745	753	760	768	775	782	5	4
586	790	797	805	812	819	827	834	842	849	856	6	4
587	864	871	879	886	893	901	908	916	923	930	7	5
588	938	945	953	960	967	975	982	989	997	*004	8	6
589	77 012	019	026	034	041	048	056	063	070	078	9	6
590	085	093	100	107	115	122	129	137	144	151		
591	159	166	173	181	188	195	203	210	217	225		
592	232	240	247	254	262	269	276	283	291	298		
593	305	313	320	327	335	342	349	357	364	371		
594	379	386	393	401	408	415	422	430	437	444		
595	452	459	466	474	481	488	495	503	510	517		
596	525	532	539	546	554	561	568	576	583	590		
597	597	605	612	619	627	634	641	648	656	663		
598	670	677	685	692	699	706	714	721	728	735		
599	743	750	757	764	772	779	786	793	801	808		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
600	77 815	822	830	837	844	851	859	866	873	880		
601	887	895	902	909	916	924	931	938	945	952		
602	960	967	974	981	988	996	*003	*010	*017	*025		
603	78 032	039	046	053	061	068	075	082	089	097		
604	104	111	118	125	132	140	147	154	161	168		
605	176	183	190	197	204	211	219	226	233	240		
606	247	254	262	269	276	283	290	297	305	312		**8**
607	319	326	333	340	347	355	362	369	376	383	1	1
608	390	398	405	412	419	426	433	440	447	455	2	2
609	462	469	476	483	490	497	504	512	519	526	3	2
											4	3
610	533	540	547	554	561	569	576	583	590	597	5	4
611	604	611	618	625	633	640	647	654	661	668	6	5
612	675	682	689	696	704	711	718	725	732	739	7	6
613	746	753	760	767	774	781	789	796	803	810	8	6
614	817	824	831	838	845	852	859	866	873	880	9	7
615	888	895	902	909	916	923	930	937	944	951		
616	958	965	972	979	986	993	*000	*007	*014	*021		
617	79 029	036	043	050	057	064	071	078	085	092		
618	099	106	113	120	127	134	141	148	155	162		
619	169	176	183	190	197	204	211	218	225	232		
620	239	246	253	260	267	274	281	288	295	302		
621	309	316	323	330	337	344	351	358	365	372		**7**
622	379	386	393	400	407	414	421	428	435	442	1	1
623	449	456	463	470	477	484	491	498	505	511	2	1
624	518	525	532	539	546	553	560	567	574	581	3	2
											4	3
625	588	595	602	609	616	623	630	637	644	650	5	4
626	657	664	671	678	685	692	699	706	713	720	6	4
627	727	734	741	748	754	761	768	775	782	789	7	5
628	796	803	810	817	824	831	837	844	851	858	8	6
629	865	872	879	886	893	900	906	913	920	927	9	6
630	934	941	948	955	962	969	975	982	989	996		
631	80 003	010	017	024	030	037	044	051	058	065		
632	072	079	085	092	099	106	113	120	127	134		
633	140	147	154	161	168	175	182	188	195	202		
634	209	216	223	229	236	243	250	257	264	271		
635	277	284	291	298	305	312	318	325	332	339		
636	346	353	359	366	373	380	387	393	400	407		**6**
637	414	421	428	434	441	448	455	462	468	475	1	1
638	482	489	496	502	509	516	523	530	536	543	2	1
639	550	557	564	570	577	584	591	598	604	611	3	2
											4	2
640	618	625	632	638	645	652	659	665	672	679	5	3
641	686	693	699	706	713	720	726	733	740	747	6	4
642	754	760	767	774	781	787	794	801	808	814	7	4
643	821	828	835	841	848	855	862	868	875	882	8	5
644	889	895	902	909	916	922	929	936	943	949	9	5
645	956	963	969	976	983	990	996	*003	*010	*017		
646	81 023	030	037	043	050	057	064	070	077	084		
647	090	097	104	111	117	124	131	137	144	151		
648	158	164	171	178	184	191	198	204	211	218		
649	224	231	238	245	251	258	265	271	278	285		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
650	81 291	298	305	311	318	325	331	338	345	351		
651	358	365	371	378	385	391	398	405	411	418		
652	425	431	438	445	451	458	465	471	478	485		
653	491	498	505	511	518	525	531	538	544	551		
654	558	564	571	578	584	591	598	604	611	617		
655	624	631	637	644	651	657	664	671	677	684		
656	690	697	704	710	717	723	730	737	743	750		
657	757	763	770	776	783	790	796	803	809	816		
658	823	829	836	842	849	856	862	869	875	882		
659	889	895	902	908	915	921	928	935	941	948		
660	954	961	968	974	981	987	991	*000	*007	*014		7
661	82 020	027	033	040	046	053	060	066	073	079	1	1
662	086	092	099	105	112	119	125	132	138	145	2 1	
663	151	158	164	171	178	184	191	197	204	210	3 2	
664	217	223	230	236	243	249	256	263	269	276	4 3	
665	282	289	295	302	308	315	321	328	334	341	5 4	
666	347	354	360	367	373	380	387	393	400	406	6 4	
667	413	419	426	432	439	445	452	458	465	471	7 5	
668	478	484	491	497	504	510	517	523	530	536	8 6	
669	543	549	556	562	569	575	582	588	595	601	9 6	
670	607	614	620	627	633	640	646	653	659	666		
671	672	679	685	692	698	705	711	718	724	730		
672	737	743	750	756	763	769	776	782	789	795		
673	802	808	814	821	827	834	840	847	853	860		
674	866	872	879	885	892	898	905	911	918	924		
675	930	937	943	950	956	963	969	975	982	988		
676	995	*001	*008	*014	*020	*027	*033	*040	*046	*052		
677	83 059	065	072	078	085	091	097	104	110	117		
678	123	129	136	142	149	155	161	168	174	181		
679	187	193	200	206	213	219	225	232	238	245		
680	251	257	264	270	276	283	289	296	302	308		
681	315	321	327	334	340	347	353	359	366	372		6
682	378	385	391	398	404	410	417	423	429	436	1	1
683	442	448	455	461	467	474	480	487	493	499	2 1	
684	506	512	518	525	531	537	544	550	556	563	3 2	
685	569	575	582	588	594	601	607	613	620	626	4 2	
686	632	639	645	651	658	664	670	677	683	689	5 3	
687	696	702	708	715	721	727	734	740	746	753	6 4	
688	759	765	771	778	784	790	797	803	809	816	7 4	
689	822	828	835	841	847	853	860	866	872	879	8 5	
											9 5	
690	885	891	897	904	910	916	923	929	935	942		
691	948	954	960	967	973	979	985	992	998	*004		
692	84 011	017	023	029	036	042	048	055	061	067		
693	073	080	086	092	098	105	111	117	123	130		
694	136	142	148	155	161	167	173	180	186	192		
695	198	205	211	217	223	230	236	242	248	255		
696	261	267	273	280	286	292	298	305	311	317		
697	323	330	336	342	348	354	361	367	373	379		
698	386	392	398	404	410	417	423	429	435	442		
699	448	454	460	466	473	479	485	491	497	504		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9
700	84 510	516	522	528	535	541	547	553	559	566
701	572	578	584	590	597	603	609	615	621	628
702	634	640	646	652	658	665	671	677	683	689
703	696	702	708	714	720	726	733	739	745	751
704	757	763	770	776	782	788	794	800	807	813
705	819	825	831	837	844	850	856	862	868	874
706	880	887	893	899	905	911	917	924	930	936
707	942	948	954	960	967	973	979	985	991	997
708	85 003	009	016	022	028	034	040	046	052	058
709	065	071	077	083	089	095	101	107	114	120
710	126	132	138	144	150	156	163	169	175	181
711	187	193	199	205	211	217	224	230	236	242
712	248	254	260	266	272	278	285	291	297	303
713	309	315	321	327	333	339	345	352	358	364
714	370	376	382	388	394	400	406	412	418	425
715	431	437	443	449	455	461	467	473	479	485
716	491	497	503	509	516	522	528	534	540	546
717	552	558	564	570	576	582	588	594	600	606
718	612	618	625	631	637	643	649	655	661	667
719	673	679	685	691	697	703	709	715	721	727
720	733	739	745	751	757	763	769	775	781	788
721	794	800	806	812	818	824	830	836	842	848
722	854	860	866	872	878	884	890	896	902	908
723	914	920	926	932	938	944	950	956	962	968
724	974	980	986	992	998	*004	*010	*016	*022	*028
725	86 034	040	046	052	058	064	070	076	082	088
726	094	100	106	112	118	124	130	136	141	147
727	153	159	165	171	177	183	189	195	201	207
728	213	219	225	231	237	243	249	255	261	267
729	273	270	285	291	297	303	308	314	320	326
730	332	338	344	350	356	362	368	374	380	386
731	392	398	404	410	415	421	427	433	439	445
732	451	457	463	469	475	481	487	493	499	504
733	510	516	522	528	534	540	546	552	558	564
734	570	576	581	587	593	599	605	611	617	623
735	629	635	641	646	652	658	664	670	676	682
736	688	694	700	705	711	717	723	729	735	741
737	747	753	759	764	770	776	782	788	794	800
738	806	812	817	823	829	835	841	847	853	859
739	864	870	876	882	888	894	900	906	911	917
740	923	929	935	941	947	953	958	964	970	976
741	982	988	994	999	*005	*011	*017	*023	*029	*035
742	87 040	046	052	058	064	070	075	081	087	093
743	099	105	111	116	122	128	134	140	146	151
744	157	163	169	175	181	186	192	198	204	210
745	216	221	227	233	239	245	251	256	262	268
746	274	280	286	291	297	303	309	315	320	326
747	332	338	344	349	355	361	367	373	379	384
748	390	396	402	408	413	419	425	431	437	442
749	448	454	460	466	471	477	483	439	495	500

P. P.

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9	6	9	5	9	5

N.	0	1	2	3	4	5	6	7	8	9	P. P.

LOGARITHMS OF NUMBERS — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
750	87 506	512	518	523	529	535	541	547	552	558		
751	564	570	576	581	587	593	599	604	610	616		
752	622	628	633	639	645	651	656	662	668	674		
753	679	685	691	697	703	708	714	720	726	731		
754	737	743	749	754	760	766	772	777	783	789		
755	795	800	806	812	818	823	829	835	841	846		
756	852	858	864	869	875	881	887	892	898	904		
757	910	915	921	927	933	938	944	950	955	961		
758	967	973	978	984	990	996	*001	*007	*013	*018		
759	88 024	030	036	041	047	053	058	064	070	076		
760	081	087	093	098	104	110	116	121	127	133		
761	138	144	150	156	161	167	173	178	184	190		6
762	195	201	207	213	218	224	230	235	241	247	1	1
763	252	258	264	270	275	281	287	292	298	304	2	1
764	309	315	321	326	332	338	343	349	355	360	3	2
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765	366	372	377	383	389	395	400	406	412	417	5	3
766	423	429	434	440	446	451	457	463	468	474	6	4
767	480	485	491	497	502	508	513	519	525	530	7	4
768	536	542	547	553	559	564	570	576	581	587	8	5
769	593	598	604	610	615	621	627	632	638	643	9	5
770	649	655	660	666	672	677	683	689	694	700		
771	705	711	717	722	728	734	739	745	750	756		
772	762	767	773	779	784	790	795	801	807	812		
773	818	824	829	835	840	846	852	857	863	868		
774	874	880	885	891	897	902	908	913	919	925		
775	930	936	941	947	953	958	964	969	975	981		
776	986	992	997	*003	*009	*014	*020	*025	*031	*037		
777	89 042	048	053	059	064	070	076	081	087	092		
778	098	104	109	115	120	126	131	137	143	148		
779	154	159	165	170	176	182	187	193	198	204		
780	209	215	221	226	232	237	243	248	254	260		
781	265	271	276	282	287	293	298	304	310	315		5
782	321	326	332	337	343	348	354	360	365	371	1	1
783	376	382	387	393	398	404	409	415	421	426	2	1
784	* 432	437	443	448	454	459	465	470	476	481	3	2
											4	2
785	487	492	498	504	509	515	520	526	531	537	5	3
786	542	548	553	559	564	570	575	581	586	592	6	3
787	597	603	609	614	620	625	631	636	642	647	7	4
788	653	658	664	669	675	680	686	691	697	702	8	4
789	708	713	719	724	730	735	741	746	752	757	9	5
790	763	768	774	779	785	790	796	801	807	812		
791	818	823	829	834	840	845	851	856	862	867		
792	873	878	883	889	894	900	905	911	916	922		
793	927	933	938	944	949	955	960	966	971	977		
794	982	988	993	998	*004	*009	*015	*020	*026	*031		
795	90 037	042	048	053	059	064	069	075	080	086		
796	091	097	102	108	113	119	124	129	135	140		
797	146	151	157	162	168	173	179	184	189	195		
798	200	206	211	217	222	227	233	238	244	249		
799	255	260	266	271	276	282	287	293	298	304		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
800	90 309	314	320	325	331	336	342	347	352	358		
801	363	369	374	380	385	390	396	401	407	412		
802	417	423	428	434	439	445	450	455	461	466		
803	472	477	482	488	493	499	504	509	515	520		
804	526	531	536	542	547	553	558	563	569	574		
805	580	585	590	596	601	607	612	617	623	628		
806	634	639	644	650	655	660	666	671	677	682		
807	687	693	698	703	709	714	720	725	730	736		
808	741	747	752	757	763	768	773	779	784	789		
809	795	800	806	811	816	822	827	832	838	843		
810	849	854	859	865	870	875	881	886	891	897		
811	902	907	913	918	924	929	934	940	945	950		**6**
812	956	961	966	972	977	982	988	993	998	*004	1	1
813	91 009	014	020	025	030	036	041	046	052	057	2	1
814	062	068	073	078	084	089	094	100	105	110	3	2
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815	116	121	126	132	137	142	148	153	158	164	5	3
816	169	174	180	185	190	196	201	206	212	217	6	4
817	222	228	233	238	243	249	254	259	265	270	7	4
818	275	281	286	291	297	302	307	312	318	323	8	5
819	328	334	339	344	350	355	360	365	371	376	9	5
820	381	387	392	397	403	408	413	418	424	429		
821	434	440	445	450	455	461	466	471	477	482		
822	487	492	498	503	508	514	519	524	529	535		
823	540	545	551	556	561	566	572	577	582	587		
824	593	598	603	609	614	619	624	630	635	640		
825	645	651	656	661	666	672	677	682	687	693		
826	698	703	709	714	719	724	730	735	740	745		
827	751	756	761	766	772	777	782	787	793	798		
828	803	808	814	819	824	829	834	840	845	850		
829	855	861	866	871	876	882	887	892	897	903		
830	908	913	918	924	929	934	939	944	950	955		
831	960	965	971	976	981	986	991	997	*002	*007		**5**
832	92 012	018	023	028	033	038	044	049	054	059	1	1
833	065	070	075	080	085	091	096	101	106	111	2	1
834	117	122	127	132	137	143	148	153	158	163	3	2
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835	169	174	179	184	189	195	200	205	210	215	5	3
836	221	226	231	236	241	247	252	257	262	267	6	3
837	273	278	283	288	293	298	304	309	314	319	7	4
838	324	330	335	340	345	350	355	361	366	371	8	4
839	376	381	387	392	397	402	407	412	418	423	9	5
840	428	433	438	443	449	454	459	464	469	474		
841	480	485	490	495	500	505	511	516	521	526		
842	531	536	542	547	552	557	562	567	572	578		
843	583	588	593	598	603	609	614	619	624	629		
844	634	639	645	650	655	660	665	670	675	681		
845	686	691	696	701	706	711	716	722	727	732		
846	737	742	747	752	758	763	768	773	778	783		
847	788	793	799	804	809	814	819	824	829	834		
848	840	845	850	855	860	865	870	875	881	886		
849	891	896	901	906	911	916	921	927	932	937		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

LOGARITHMS OF NUMBERS — *Continued*

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850	92 942	947	952	957	962	967	973	978	983	988		
851	993	998	*003	*008	*013	*018	*024	*029	*034	*039		
852	93 044	049	054	059	064	069	075	080	085	090		
853	095	100	105	110	115	120	125	131	136	141		
854	146	151	156	161	166	171	176	181	186	192		
855	197	202	207	212	217	222	227	232	237	242		
856	247	252	258	263	268	273	278	283	288	293		**6**
857	298	303	308	313	318	323	328	334	339	344	1	1
858	349	354	359	364	369	374	379	384	389	394	2	1
859	399	404	409	414	420	425	430	435	440	445	3	2
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860	450	455	460	465	470	475	480	485	490	495	5	3
861	500	505	510	515	520	526	531	536	541	546	6	4
862	551	556	561	566	571	576	581	586	591	596	7	4
863	601	606	611	616	621	626	631	636	641	646	8	5
864	651	656	661	666	671	676	682	687	692	697	9	5
865	702	707	712	717	722	727	732	737	742	747		
866	752	757	762	767	772	777	782	787	792	797		
867	802	807	812	817	822	827	832	837	842	847		
868	852	857	862	867	872	877	882	887	892	897		
869	902	907	912	917	922	927	932	937	942	947		
870	952	957	962	967	972	977	982	987	992	997		
871	94 002	007	012	017	022	027	032	037	042	047		**5**
872	052	057	062	067	072	077	082	086	091	096	1	1
873	101	106	111	116	121	126	131	136	141	146	2	1
874	151	156	161	166	171	176	181	186	191	196	3	2
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875	201	206	211	216	221	226	231	236	240	245	5	3
876	250	255	260	265	270	275	280	285	290	295	6	3
877	300	305	310	315	320	325	330	335	340	345	7	4
878	349	354	359	364	369	374	379	384	389	394	8	4
879	399	404	409	414	419	424	429	433	438	443	9	5
880	448	453	458	463	468	473	478	483	488	493		
881	498	503	507	512	517	522	527	532	537	542		
882	547	552	557	562	567	571	576	581	586	591		
883	596	601	606	611	616	621	626	630	635	640		
884	645	650	655	660	665	670	675	680	685	689		
885	694	699	704	709	714	719	724	729	734	738		
886	743	748	753	758	763	768	773	778	783	787		**4**
887	792	797	802	807	812	817	822	827	832	836	1	0
888	841	846	851	856	861	866	871	876	880	885	2	1
889	890	895	900	905	910	915	919	924	929	934	3	1
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890	939	944	949	954	959	963	968	973	978	983	5	2
891	988	993	998	*002	*007	*012	*017	*022	*027	*032	6	2
892	95 036	041	046	051	056	061	066	071	075	080	7	3
893	085	090	095	100	105	109	114	119	124	129	8	3
894	134	139	143	148	153	158	163	168	173	177	9	4
895	182	187	192	197	202	207	211	216	221	226		
896	231	236	240	245	250	255	260	265	270	274		
897	279	284	289	294	299	303	308	313	318	323		
898	328	332	337	342	347	352	357	361	366	371		
899	376	381	386	390	395	400	405	410	415	419		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

LOGARITHMS OF NUMBERS — *Continued*

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901	472	477	482	487	492	497	501	506	511	516
902	521	525	530	535	540	515	550	554	559	564
903	569	574	578	583	588	593	598	602	607	612
904	617	622	626	631	636	641	646	650	655	660
905	665	670	674	679	684	689	694	698	703	708
906	713	718	722	727	732	737	742	746	751	756
907	761	766	770	775	780	785	789	794	799	804
908	809	813	818	823	828	832	837	842	847	852
909	856	861	866	871	875	880	885	890	895	899
910	904	909	914	918	923	928	933	938	942	947
911	952	957	961	966	971	976	980	985	990	995
912	999	*004	*009	*014	*019	*023	*028	*033	*038	*042
913	96 047	052	057	061	066	071	076	080	085	090
914	095	099	104	109	114	118	123	128	133	137
915	142	147	152	156	161	166	171	175	180	185
916	190	194	199	204	209	213	218	223	227	232
917	237	242	246	251	256	261	265	270	275	280
918	284	289	294	298	303	308	313	317	322	327
919	332	336	341	346	350	355	360	365	369	374
920	379	384	388	393	398	402	407	412	417	421
921	426	431	435	440	445	450	454	459	464	468
922	473	478	483	487	492	497	501	506	511	515
923	520	525	530	534	539	544	548	553	558	562
924	567	572	577	581	586	591	595	600	605	609
925	614	619	624	628	633	638	642	647	652	656
926	661	666	670	675	680	685	689	694	699	703
927	708	713	717	722	727	731	736	741	745	750
928	755	759	764	769	774	778	783	788	792	797
929	802	806	811	816	820	825	830	834	839	844
930	848	853	858	862	867	872	876	881	886	890
931	895	900	904	909	914	918	923	928	932	937
932	942	946	951	956	960	965	970	974	979	984
933	988	993	997	*002	*007	*011	*016	*021	*025	*030
934	97 035	039	044	049	053	058	063	067	072	077
935	081	086	090	095	100	104	109	114	118	123
936	128	132	137	142	146	151	155	160	165	169
937	174	179	183	188	192	197	202	206	211	216
938	220	225	230	234	239	243	248	253	257	262
939	267	271	276	280	285	290	294	299	304	308
940	313	317	322	327	331	336	340	345	350	354
941	359	364	368	373	377	382	387	391	396	400
942	405	410	414	419	424	428	433	437	442	447
943	451	456	460	465	470	474	479	483	488	493
944	497	502	506	511	516	520	525	529	534	539
945	543	548	552	557	562	566	571	575	580	585
946	589	594	598	603	607	612	617	621	626	630
947	635	640	644	649	653	658	663	667	672	676
948	681	685	690	695	699	704	708	713	717	722
949	727	731	736	740	745	749	754	759	763	768

P. P.

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6	2
7	3
8	3
9	4

N.	0	1	2	3	4	5	6	7	8	9	P. P.

Logarithms of Numbers — *Continued*

N.	0	1	2	3	4	5	6	7	8	9	P. P.	
950	97 772	777	782	786	791	795	800	804	809	813		
951	818	823	827	832	836	841	845	850	855	859		
952	864	868	873	877	882	886	891	896	900	905		
953	909	914	918	923	928	932	937	941	946	950		
954	955	959	964	968	973	978	982	987	991	996		
955	98 000	005	009	014	019	023	028	032	037	041		
956	046	050	055	059	064	068	073	078	082	087		
957	091	096	100	105	109	114	118	123	127	132		
958	137	141	146	150	155	159	164	168	173	177		
959	182	186	191	195	200	204	209	214	218	223		
960	227	232	236	241	245	250	254	259	263	268		
961	272	277	281	286	290	295	299	304	308	313		**5**
962	318	322	327	331	336	340	345	349	354	358	1	1
963	363	367	372	376	381	385	390	394	399	403	2	1
964	408	412	417	421	426	430	435	439	444	448	3	2
											4	2
965	453	457	462	466	471	475	480	484	489	493	5	3
966	498	502	507	511	516	520	525	529	534	538	6	3
967	543	547	552	556	561	565	570	574	579	583	7	4
968	588	592	597	601	605	610	614	619	623	628	8	4
969	632	637	641	646	650	655	659	664	668	673	9	5
970	677	682	686	691	695	700	704	709	713	717		
971	722	726	731	735	740	744	749	753	758	762		
972	767	771	776	780	784	789	793	798	802	807		
973	811	816	820	825	829	834	838	843	847	851		
974	856	860	865	869	874	878	883	887	892	896		
975	900	905	909	914	918	923	927	932	936	941		
976	945	949	954	958	963	967	972	976	981	985		
977	989	994	998	*003	*007	*012	*016	*021	*025	*029		
978	99 034	038	043	047	052	056	061	065	069	074		
979	078	083	087	092	096	100	105	109	114	118		
980	123	127	131	136	140	145	149	154	158	162		
981	167	171	176	180	185	189	193	198	202	207		**4**
982	211	216	220	224	229	233	238	242	247	251	1	0
983	255	260	264	269	273	277	282	286	291	295	2	1
984	300	304	308	313	317	322	326	330	335	339	3	1
											4	2
985	344	348	352	357	361	366	370	374	379	383	5	2
986	388	392	396	401	405	410	414	419	423	427	6	2
987	432	436	441	445	449	454	458	463	467	471	7	3
988	476	480	484	489	493	498	502	506	511	515	8	3
989	520	524	528	533	537	542	546	550	555	559	9	4
990	564	568	572	577	581	585	590	594	599	603		
991	607	612	616	621	625	629	634	638	642	647		
992	651	656	660	664	669	673	677	682	686	691		
993	695	699	704	708	712	717	721	726	730	734		
994	739	743	747	752	756	760	765	769	774	778		
995	782	787	791	795	800	804	808	813	817	822		
996	826	830	835	839	843	848	852	856	861	865		
997	870	874	878	883	887	891	896	900	904	909		
998	913	917	922	926	930	935	939	944	948	952		
999	957	961	965	970	974	978	983	987	991	996		
N.	0	1	2	3	4	5	6	7	8	9	P. P.	

542. SPECIFIC GRAVITY OF ACETIC ACID AT 15°

A. C. OUDEMANS[2]

CH₃·COOH, Mol. Wt. = 60.032

Specific Gravity At $\frac{15°}{15°}$	Percent CH₃·COOH	Grams, CH₃·COOH Per Liter	Molarity
1.004	3	30.1	0.50
1.008	6	60.5	1.01
1.013	9	91.2	1.52
1.017	12	122.0	2.04
1.021	15	153.2	2.56
1.026	18	184.7	3.08
1.030	21	216.3	3.60
1.034	24	248.2	4.14
1.038	27	280.3	4.68
1.041	30	312.3	5.20
1.045	33	344.9	5.75
1.048	36	377.3	6.28
1.051	39	409.9	6.84
1.054	42	442.7	7.36
1.057	45	475.6	7.93
1.060	48	508.8	8.48
1.062	51	541.6	9.04
1.065	54	575.1	9.59
1.067	57	608.2	10.30
1.069	60	641.4	10.70
1.070	62	663.3	11.04
1.071	64	685.5	11.41
1.072	66	707.5	11.81
1.073	68	729.7	12.17
1.073	70	751.1	12.51
1.074	72	773.3	12.89
1.074	74	794.8	13.25
1.075	76	817.0	13.62
1.075	78	838.5	13.97
1.075	80	860.0	14.34
1.075	82	881.5	14.70
1.074	84	902.2	15.02
1.074	86	923.6	15.39
1.073	88	944.3	15.73
1.071	90	963.9	16.06
1.070	92	984.4	16.40
1.067	94	1003.0	16.72
1.064	96	1021.5	17.02
1.060	98	1038.8	17.30
1.058	99	1047.5	17.46
1.055	100	1055.0	17.59

[2] *Zeit. f. Chem.* **9**, 751 (1866).

543. Specific Gravity of Hydrochloric Acid at 15°

G. Lunge and L. Marchlewski [8]

HCl, Mol. Wt. = 36.465

Specific Gravity At $\frac{15°}{4°}$	Percent HCl	Grams, HCl Per Liter	Molarity
1.000	0.16	1.6	0.04
1.005	1.15	12	0.33
1.010	2.14	22	0.60
1.015	3.12	32	0.88
1.020	4.13	42	1.15
1.025	5 15	53	1.45
1.030	6.15	64	1.75
1.035	7.15	74	2.03
1.040	8.16	85	2.33
1.045	9.16	96	2.63
1.050	10.17	107	2.93
1.055	11.18	118	3.24
1.060	12.19	129	3.54
1.065	13.19	141	3.86
1.070	14.17	152	4.17
1.075	15 16	163	4.47
1.080	16.15	174	4.77
1.085	17.13	186	5.10
1.090	18.11	197	5.40
1.095	19.06	209	5.73
1.100	20.01	220	6.03
1.105	20.97	232	6.35
1.110	21.92	243	6.66
1.115	22.86	255	6.98
1.120	23.82	267	7.30
1.125	24.78	278	7.62
1.130	25.75	291	7.97
1.135	26.70	303	8.30
1.140	27.66	315	8.64
1.145	28.61	328	8.99
1.150	29.57	340	9.32
1.155	30.55	353	9.68
1.160	31.52	366	10.03
1.165	32.49	379	10.40
1.170	33.46	392	10.73
1.175	34.42	404	11.07
1.180	35.39	418	11.48
1.185	36.31	430	11.80
1.190	37.23	443	12.15
1.195	38.16	456	12.50
1.200	39.11	469	12.86

[8] *Z. angew. Chem.* **4,** 135 (1891).

544.   Specific Gravity of Nitric Acid at 15°

G. Lunge and H. Rey [4]

HNO₃, Mol. Wt. = 63.016

Specific Gravity At $\frac{15°}{4°}$	Percent HNO₃	Grams, HNO₃ Per Liter	Molarity
1.000	0.10	1	0.02
1.020	3.70	38	0.60
1.040	7.26	75	1.19
1.060	10.68	113	1.80
1.080	13.95	151	2.40
1.100	17.11	188	2.98
1.120	20.23	227	3.60
1.140	23.31	266	4.22
1.160	26.36	306	4.86
1.180	29.38	347	5.51
1.200	32.36	388	6.61
1.220	35.28	430	6.83
1.240	38.29	475	7.54
1.260	41.34	521	8.27
1.280	44.41	568	9.03
1.300	47.49	617	9.80
1.320	50.71	669	10.62
1.340	54.07	725	11.50
1.350	55.79	753	11.96
1.360	57 57	783	12.44
1.370	59.39	814	12.93
1.380	61 27	846	13.43
1.390	63.23	879	14.13
1.400	65.30	914	14.50
1.410	67.50	952	15.12
1.420	69.80	991	15.73
1.430	72.17	1032	16.40
1.440	74.68	1075	17.08
1.450	77.28	1121	17.80
1.460	79.98	1168	18.55
1.470	82.90	1219	19.34
1.480	86.05	1274	20.23
1.490	89.60	1335	21.20
1.500	94.09	1411	22.40
1.505	96.39	1451	23.00
1.510	98.10	1481	23.50
1.512	98.53	1490	23.65
1.514	98.90	1497	23.75
1.516	99.21	1504	23.90
1.518	99.46	1510	24.00
1.520	99.67	1515	24.05

[4] Z. angew. Chem. **4**, 165 (1891).

545. SPECIFIC GRAVITY OF PHOSPHORIC ACID AT 17.5°

HAGER [5]

H_3PO_4, Mol. Wt. = 98.051

Specific Gravity	Percent H_3PO_4	Grams, H_3PO_4 Per Liter	Molarity
1.017	3.44	35.0	0.36
1.033	6.20	64.0	0.65
1.049	8.95	93.9	0.96
1.066	11.71	124.2	1.27
1.083	14.46	156.6	1.59
1.100	17.22	189.4	1.93
1.118	19.97	223.3	2.28
1.135	22.73	257.9	2.64
1.155	25.48	294.4	3.00
1.174	28.24	331.4	3.38
1.193	30.99	369.7	3.78
1.213	33.75	409.3	4.17
1.233	36.50	450.0	4.59
1.255	39.26	492.6	5.03
1.276	42.01	536.1	5.48
1.298	44.77	581.0	5.94
1.319	47.52	626.7	6.40
1.342	50.28	674.8	6.89
1.365	53.04	723.9	7.38
1.389	55.79	774.9	8.02
1.415	58.55	828.5	8.46
1.441	61.30	883.5	9.02
1.469	64.06	941.6	9.62
1.498	66.81	1001.1	10.21
1.528	69.57	1063.7	10.86
1.559	72.32	1127.2	11.50
1.589	75.08	1193.3	12.19
1.605	76.45	1227.5	12.51
1.621	77.83	1261.3	12.88
1.637	79.21	1296.1	13.22
1.653	80.59	1332.9	13.60
1.669	81.97	1367.7	13.93
1.685	83.34	1404.4	14.33
1.701	84.72	1440.2	14.70
1.717	86.10	1478.0	15.10
1.733	87.48	1516.8	15.46
1.750	88.85	1554.5	15.88
1.766	90.23	1593.3	16.26
1.783	91.61	1634.1	16.70
1.800	92.99	1673.9	17.10
1.809	93.67	1693.7	17.30

[5] *Manuale Pharm.* Leipzig, 1876.

546.   Specific Gravity of Sulfuric Acid at 15°

G. Lunge and M. Isler [6]

H_2SO_4, Mol. Wt. = 98.080

Specific Gravity At $\frac{15°}{4°}$	Percent H_2SO_4	Grams, H_2SO_4 Per Liter	Molarity
1.020	3.03	31	0.32
1.060	8.77	93	0.95
1.080	11.60	125	1.27
1.100	14.35	158	1.61
1.120	17.01	191	1.95
1.140	19.61	223	2.27
1.160	22.19	257	2.62
1.180	24.76	292	2.98
1.200	27.32	328	3.34
1.220	29.84	364	3.71
1.240	32.28	400	4.08
1.260	34.57	435	4.44
1.280	36.87	472	4.81
1.300	39.19	510	5.20
1.320	41.50	548	5.59
1.340	43.74	586	5.97
1.360	45.88	624	6.36
1.380	48.00	662	6.75
1.400	50.11	702	7.15
1.420	52.15	740	7.54
1.440	54.07	779	7.94
1.460	55.97	817	8.32
1.480	57.83	856	8.72
1.500	59.70	896	9.13
1.520	61.59	936	9.54
1.540	63.43	977	9.96
1.560	65.08	1015	10.35
1.580	66.71	1054	10.74
1.600	68.51	1096	11.17
1.620	70.32	1139	11.61
1.640	71.99	1181	12.04
1.660	73.64	1222	12.45
1.680	75.42	1267	12.91
1.700	77.17	1312	13.37
1.720	78.92	1357	13.83
1.740	80.68	1404	14.31
1.760	82.44	1451	14.79
1.780	84.50	1504	15.33
1.800	86.90	1564	15.94
1.820	90.05	1639	16.71
1.841	97.00	1786	17.20
1.839	99.70	1834	18.69

[6] *Z. angew. Chem.* **3,** 131 (1890).

547. Specific Gravity of Aqua Ammonia at 15°

G. Lunge and T. Wiernik [7]

NH_3, Mol. Wt. = 17.032

Specific Gravity At $\frac{15°}{-0}$	Percent NH_3	Grams, NH_3 Per Liter	Molarity
1.000	0.00	0.0	0.00
0.996	0.91	9.1	0.54
0.992	1.84	18.2	1.07
0.988	2.80	27.7	1.63
0.984	3.80	37.4	2.20
0.980	4.80	47.0	2.76
0.976	5.80	56.6	3.33
0.972	6.80	66.1	3.88
0.968	7.82	75.7	4.45
0.964	8.84	85.2	5.01
0.960	9.91	95.1	5.60
0.956	11.03	105.4	6.21
0.952	12.17	115.9	6.82
0.948	13.31	126.2	7.43
0.944	14.46	136.5	8.03
0.940	15.63	146.9	8.64
0.936	16.82	157.4	9.26
0.932	18.03	168.1	9.88
0.928	19.25	178.6	10.50
0.924	20.49	189.3	11.13
0.922	21.12	194.7	11.43
0.920	21.75	200.1	11.77
0.918	22.39	205.6	12.10
0.916	23.03	210.9	12.41
0.914	23.68	216.3	12.72
0.912	24.33	221.9	13.06
0.910	24.99	227.4	13.39
0.908	25.65	232.9	13.70
0.906	26.31	238.3	13.96
0.904	26.98	243.9	14.37
0.902	27.65	249.4	14.70
0.900	28.33	255.0	15.00
0.898	29.01	260.5	15.32
0.896	29.69	266.0	15.66
0.894	30.37	271.5	15.97
0.892	31.05	277.0	16.30
0.890	31.75	282.6	16.63
0.888	32.50	288.6	16.98
0.886	33.25	294.6	17.32
0.884	34.10	301.4	17.73
0.882	34.95	308.3	18.14

[7] Z. angew. Chem. **2**, 181 (1889).

548.   SOLUBILITY OF GASES IN WATER

GRAMS PER LITER OF SOLVENT

When Partial Pressure of the Gas + Vapor Pressure of the Liquid = 760 mm.
at the Respective Temperatures

T.	Oxygen[8]	Hydrogen[9]	Nitrogen[10]	Air[11]
0	0.0695	0.0019	0.029	0.039
10	.0537	.0017	.023	.029
20	.0434	.0016	.019	.024
30	.0359	.0015	.016	.020
40	.0308	.0014	.014	.017
50	.0266	.0013	.012	.015
60	.0227	.0012	.011	.013
70	.0186	.0010	.009	.011
80	.0138	.0008	.007	.008
90	.0079	.0005	.004	.005
100	.0000	.0000	.000	.000

T.	Chlorine[12]	Carbon Dioxide[13]	Hydrogen Sulfide[14]	Sulfur Dioxide[15]
0	. . . .	3.347	7.066	228.3
10	9.972	2.319	5.112	162.1
20	7.293	1.689	3.846	112.9
30	5.723	1.259	2.983	78.1
40	4.590	0.974	2.361	54.1
50	3.925	0.762	1.883	. . . .
60	3.295	0.577	1.480	. . . .
70	2.793	. . . .	1.101	. . . .
80	2.227	. . . .	0.765	. . . .
90	1.270	. . . .	0.410	. . . .
100	0.000	. . . .	0.000	. . . .

[8] L. W. Winkler, *Ber.* **22**, 1772 (1889).
[9] L. W. Winkler, *ibid.* **24**, 99 (1891).
[10] L. W. Winkler. *ibid.* **24**, 3602 (1891).
[11] Calculated from oxygen and nitrogen solubilities.
[12] L. W. Winkler, *Matematik. és Termeszettud. Ertesitö.* **25**, 86 (1907).
[13] Chr. Bohr, *Wied. Ann.* **68**, 504 (1899).
[14] L. W. Winkler, *Matematik. és Termeszettud. Ertesitö.* **25**, 86 (1907).
[15] Franz Schönfeld, *Liebigs Ann.* **95**, 1 (1855).

549. SATURATED SOLUTIONS OF SOME REAGENTS AT 20°

Reagent	Formula	Specific Gravity	Molarity	Quantities Required for 1 Liter Saturated Solution	
				Grams of Reagent	ml. Water
Ammonium Chloride.	NH_4Cl	1.075	5.44	291	784
Ammonium Nitrate...	NH_4NO_3	1.312	10.80	863	449
Ammonium Oxalate..	$(NH_4)_2C_2O_4 \ H_2O$	1.030	0.295	48	982
Ammonium Sulfate ..	$(NH_4)_2SO_4$	1.243	4.06	535	708
Barium Chloride ...	$BaCl_2$	1.290	1.66	339	951
" "	$BaCl_2 \cdot 2H_2O$	1.290	1.63	398	892
Barium Hydroxide....	$Ba(OH)_2$	1.037	0.228	39	998
" "	$Ba(OH)_2 \cdot 8H_2O$	1.037	0.228	72	965
Calcium Hydroxide...	$Ca(OH)_2$	1.000	0.022	1.6	1000
Mercuric Chloride....	$HgCl_2$	1.050	0.236	64	986
Potassium Chloride ..	KCl	1.174	4.00	298	876
Potassium Chromate.	K_2CrO_4	1.396	3.00	583	858
Potassium Dichromate	$K_2Cr_2O_7$	1.077	0.39	115	962
Potassium Hydroxide	KOH	1.540	14.50	813	727
Sodium Carbonate ...	Na_2CO_3	1.178	1.97	209	869
" "	$Na_2CO_3 \cdot 10H_2O$	1.178	1 97	563	515
Sodium Chloride	$NaCl$	1.197	5.40	316	881
Sodium Hydroxide....	$NaOH$	1.539	20.07	803	736

550.   UNITS OF MASS

Apothecaries'

Unit	Symbol	Grains	Scruples	Drams	Ounces	Pounds	Grams
1 Grain =	gr.	1	0.05	0.01666	0.0021	0.00017	0.06479
1 Scruple =	℈	20	1.0	0.3333	0.0416	0.00347	1.2959
1 Dram =	ℨ	60	3.0	1.0	0.125	0.0¹04	3.8879
1 Ounce =	℥	480	24.0	8.0	1.0	0.0833	31.1035
1 Pound =	lb.	5760	288.0	96.0	12.0	1.0	373.2418

Avoirdupois

Unit	Symbol	Grains	Drams	Ounces	Pounds	Grams	Kilograms
1 Grain =	gr.	1.0	0.03657	0.00228	0.00014	0.06479	. . . . .
1 Dram =	dr.	27.3437	1.0	0.0625	0.0039	1.7718	. . . . .
1 Ounce =	oz.	437.5	16.0	1.0	0.0625	28.3495	. . . . .
1 Pound =	lb.	7000.0	256.0	16.0	1.0	453.5924	0.4536
1 Short Ton =	sh. tn.	. . . .	. . . .	. . . .	2000.0	. . . .	907.1848
1 Long Ton =	l. tn.	. . . .	. . . .	. . . .	2240.0	. . . .	1016.0470

Troy

Unit	Symbol	Grains	Pennyweights	Ounces	Pounds	Grams
1 Grain =	gr.	1.0	0.04166	0.0021	0.00017	0.06479
1 Pennyweight =	dwt.	24.0	1.0	0.05	0.00416	1.5552
1 Ounce =	oz.	480.0	20.0	1.0	0.0833	31.1035
1 Pound =	lb.	5760.0	240.0	12.0	1.0	373.2418

Metric

Unit	Symbol	Milligrams	Grams	Kilograms	Avoir. Pounds	Grains
1 Milligram =	mg.	1.0	0.001	0.0₅1	. . . .	0.0154
1 Gram =	g.	1,000.0	1.0	0.001	0.0022	15.4323
1 Kilogram =	kg.	1,000,000.0	1000.0	1.0	2.2046	15,432.356
1 Metric Ton =	. . . .	. . . .	. . . .	1000.0	2204.6223	. . . .

551. ## UNITS OF LIQUID CAPACITY

Apothecaries'

Unit		Symbol	Minims	Fluid Drams	Fluid Ounces	Cubic Centimeters
1 Minim	=	min. or ℥	1.0	0.0166	0.0021	0.0616
1 Fluid Dram	=	fl. dr. or ℥	60.0	1.0	0.125	3.6966
1 Fluid Ounce	=	fl. oz. or ℥	480.0	8.0	1.0	29.5729
1 Pint	=	pt. or O	7680.0	128.0	16.0	473.167

United States

Unit		Symbol	Gills	Pints	Quarts	Gallons	Cubic Centimeters	Liters
1 Gill	=	gi.	1.0	0.25	0.125	0.03125	118.292	....
1 Pint	=	pt.	4.0	1.0	0.5	0.125	473.167	....
1 Quart	=	qt.	8.0	2.0	1.0	0.25	946.333	0.9463
1 Gallon	=	gal.	32.0	8.0	4.0	1.0	3785.332	3.7853

Imperial or British

Unit		Symbol	Minims	Fluid Drams	Fluid Ounces	Pints	Gallons	Cubic Centimeters
1 Minim	=	min.	1.0	0.0166	0.0021	....	....	0.059
1 Fluid Dram	=	fl. dr.	60.0	1.0	0.125	0.00625	0.0008	3.549
1 Fluid Ounce	=	fl. oz.	480.0	8.0	1.0	0.05	0.00625	28.396
1 Pint	=	pt.	9,600.0	160.0	20.0	1.0	0.125	567.936
1 Gallon	=	gal.	76,800.0	1280.0	160.0	8.0	1.0	4543.487

Metric

Unit		Symbol	Milliliters *	Liters	Cubic* Centimeters	U. S. Gallons	Apoth. Minims	Apoth. Fluid Oz.
1 Milliliter	=	ml.	1.0	0.001	1.0	....	16.2311	....
1 Liter	=	l.	1000.0	1.0	1000.0	0.2641	....	33.815

* See § 103 for discussion on differences between milliliter and cubic centimeter.

Conversion Table

Unit		Cubic Inches	Pounds of Water At 16.7°	U. S. Gallons	Imp. Gallons	Liters	Fluid Ounces
1 U. S. Gallon	=	231.00	8.335	1.000	0.83	3.785	128.0
1 Imp. Gallon	=	277.27	10.000	1.200	1.00	4.543	160.0
1 Liter	=	61.03	2.200	0.264	0.22	1.0	33.8
1 Fluid Ounce	=	1.80	0.065	0.008	0.006	0.029	1.0

APPENDIX

552. ## UNITS OF DRY CAPACITY
United States

Unit	Symbol	Pints	Quarts	Pecks	U. S. Bushels	Imperial Bushels	Liters
1 Pint =	pt.	1.0	0.5	0.0625	0.01562	....	0.5506
1 Quart =	qt.	2.0	1.0	0.125	0.03125	....	1.1012
1 Peck =	pk.	16.0	8.0	1.0	0.25	....	8.810
1 Bushel =	bu.	64.0	32.0	4.0	1.0	0.9694	35.238

Metric

Unit	Symbol	Liters	Dekaliters	Hectoliters	Quarts	Pecks	Bushels
1 Liter =	l.	1.0	0.1	0.01	0.908	0.1135	0.0284
1 Dekaliter =	dkl.	10.0	1.0	0.1	9 081	1.135	0.2838
1 Hectoliter =	hl.	100.0	10.0	1.0	90.810	11.35	2.838

553. ## UNITS OF LENGTH
United States

Unit	Symbol	Inches	Feet	Yards	Miles*	Millimeters	Meters
1 Inch =	in.	1.0	0.0833	0.0277	0.0₄158	25.400	0.0254
1 Foot =	ft.	12.0	1.0	0 333	0.0₃189	304.801	0.3048
1 Yard =	yd.	36.0	3.0	1.0	0.0₃568	914.402	0.9144
1 Mile =	mi.	63,360.0	5280.0	1760.0	1.0	....	1609.347

*1 mile = 1.609 kilometers.

Metric

Unit	Symbol	Millimeters	Centimeters	Meters	Kilometers*	Inches	Feet
1 Ångstrom =	Å	....	10^{-8}	....	....	....	....
1 Millimicron =	mμ or μμ	....	10^{-7}	....	....	....	....
1 Micron =	μ	....	10^{-4}	....	....	....	....
1 Millimeter =	mm.	1.0	0.1	0.001	....	0.03937	0.00328
1 Centimeter =	cm.	10.0	1.0	0.01	0.0₄1	0.3937	0.0328
1 Meter =	m.	1,000.0	100.0	1.0	0.001	39.37	3.2808
1 Kilometer =	km.	1,000,000.0	100,000.0	1000.0	1.0	....	3280.833

*1 kilometer = 0.6213 miles.

Surveyors'

Unit	Links	Rods	Chains	Centimeters	Inches
1 Link =	1.0	0.04	0.0007	20.117	7.92
1 Rod =	25.0	1.0	0.25	502.921	198.00
1 Chain =	100.0	4.0	1.0	2011.684	792.00

554. ## UNITS OF AREA

United States

Unit	Symbol	Square Inches	Square Feet	Square Yards	Hectares	Square Centimeters	Square Meters
1 Square Inch =	sq. in.	1.0	0.0_69	0.0_77	....	6.451	. .
1 Square Foot =	sq. ft	144.0	1.0	0.111	....	929.034	0 0929
1 Square Yard =	sq. yd.	1296.0	9.0	1.0	....	8361.307	0.8361
1 Acre =	A.	....	43,560.0	4840.0	0.4047	....	4046.873

1 square mile = 640 acres

Metric

Unit	Symbol	Square Centimeters	Square Meters	Hectares	Square Inches	Square Feet	Acres
1 Sq. Centimeter =	sq cm	1 0	0.0_41	. .	0.155	0.00107	....
1 Square Meter =	sq. m.	10,000.0	1.0	0.0_41	1550.0	10.7638	....
1 Hectare =	ha.	....	10,000.0	1.0	....	. .	2.47104

1 square mile = 258.999 hectares

555. ## UNITS OF VOLUME

United States

Unit	Symbol	Cubic Inches	Cubic Feet	Cubic Yards	Cubic Centimeters	Cubic Decimeters	Cubic Meters
1 Cubic Inch	cu. in.	1.0	0.00058	0.00002	16.387	0.01638	0.0_16
1 Cubic Foot	cu. ft.	1,728.0	1.0	0.03704	28,317.016	28.31702	0.0283
1 Cubic Yard	cu. yd.	46,656.0	27.0	1.0	....	....	0.7645

Metric

Unit	Symbol	Cubic Centimeters	Cubic Decimeters	Cubic Meters	Cubic Inches	Cubic Feet	Cubic Yards
1 Cubic Centimeter	c.c.	1.0	0.001	0.0_51	0.061	0.0_45	0.0_51
1 Cubic Decimeter	c. dm.	1,000.0	1.0	0.001	61.023	0.0353	0.00131
1 Cubic Meter	c.m.	1,000,000.0	1,000.0	1.0	61,023.38	35.3144	1.3079

556.   UNITS OF WIRE MEASURE

Unit of Diameter of Wire

Unit	Symbol	Mils	Inches	Millimeters
1 Mil =	mil	1.0	0.001	0.0254
1 Inch =	in.	1000.0	1.0	....
1 Millimeter =	mm.	39.37	....	1.0

Unit of Cross Section Area of Wire

Unit	Symbol	Circular Mils	Square Mils	Square Inches	Square Millimeters
1 Circular Mil =	C.M.	1.0	0.7854	0.0_678	0.0_251
1 Square Mil =	sq. mil	1.273	1.0	0.0_51	0.0_264
1 Square Inch =	sq. in.	1.273×10^6	10^6	1.0	....
1 Square Millimeter =	sq. mm.	1973.0	1550.0	....	1.0

557. The Use of an Odd Number of Swings in Determining the Zero Point of a Balance. — In § 65 it was stated that the zero point of a balance will lie halfway between the average of $n + 1$ turning points on one side and n turning points on the other. To show that this is the case, let us establish the proposition for three points on the left and two on the right. The method of proof to be considered can be extended to four points on the left and three on the right or, if desired, to an even greater number of points on each side. Let us consider Figure 23 of § 65, which represents the oscillations of a balance needle plotted as a function of time. Since the oscillations are damped, the ratio of the amplitude of any vibration to the next is constant, thus if s_1, s_2, s_3, s_4, and s_5 are successive amplitudes

$$\frac{s_1}{s_2} = \frac{s_2}{s_3} = \frac{s_3}{s_4} = \frac{s_4}{s_5} = \text{constant.}$$

The value of this constant ratio is equal to $e^{\frac{aT}{2}}$ where e is the value of base 2.7218 . . . , a is related to the coefficient of friction, and T is the period of vibration in seconds. Usually, for a good analytical balance, a is very small, so that the quantity $\frac{aT}{2}$ is also small, say about 0.1, whence $e^{\frac{aT}{2}}$ is slightly greater than unity ($e^{0.1} = 1.10$). To handle matters further let us expand $e^{\frac{aT}{2}}$ into a series. We get $e^{\frac{aT}{2}} = 1 + \frac{aT}{2} + \frac{(aT)^2}{8} + \ldots$ For our purposes we need only consider the first two terms $\left(1 + \frac{aT}{2}\right)$.

We may now equate each of the several ratios $\frac{s_1}{s_2}, \frac{s_2}{s_3}, \ldots$ to $1 + \frac{aT}{2}$, whence

$$\frac{s_1}{s_2} = 1 + \frac{aT}{2}, \tag{a}$$

$$\frac{s_2}{s_3} = 1 + \frac{aT}{2}, \tag{b}$$

$$\frac{s_3}{s_4} = 1 + \frac{aT}{2}. \tag{c}$$

From (a) $s_1 = s_2\left(1 + \frac{aT}{2}\right),$ (d)

(b) $s_2 = s_3\left(1 + \frac{aT}{2}\right),$ (e)

(c) $s_3 = s_4\left(1 + \frac{aT}{2}\right).$ (f)

. . . .

Substituting the value of s_2 from (e) in (d), we get

$$s_1 = s_3\left(1 + \frac{aT}{2}\right)^2. \tag{g}$$

Substituting the value of s_3 from (f) in (g), we get

$$s_1 = s_4\left(1 + \frac{aT}{2}\right)^3, \tag{h}$$

and continuing in similar manner, we get finally

$$s_1 = s_5\left(1 + \frac{aT}{2}\right)^4,$$

$$s_2 = s_5\left(1 + \frac{aT}{2}\right)^3,$$

$$s_3 = s_5\left(1 + \frac{aT}{2}\right)^2,$$

$$s_4 = s_5\left(1 + \frac{aT}{2}\right),$$

$$s_5 = s_5.$$

Let us now obtain the average of the three amplitudes s_1, s_3, s_5 on the left and the two amplitudes s_2 and s_4 on the right.   We have for the first average

$$\frac{s_1 + s_3 + s_5}{3},$$

or, substituting values from above,

$$\frac{s_5\left(1 + \frac{aT}{2}\right)^4 + s_5\left(1 + \frac{aT}{2}\right)^2 + s_5}{3},$$

expanding the terms in parentheses and rejecting all terms higher than the first degree, since they are negligible with respect to unity, we get as the value of our expression

$$\frac{s_5\left(1 + 2\,aT\right) + s_5\left(1 + aT\right) + s_5}{3} = s_5\left(1 + aT\right).$$

Proceeding the same way for the value of the right-hand average, we have

$$\frac{s_b\left(1 + \frac{aT}{2}\right)^3 + s_b\left(1 + \frac{aT}{2}\right)}{2},$$

which is equal to

$$\frac{s_b\left(1 + 3\frac{aT}{2}\right) + s_b\left(1 + \frac{aT}{2}\right)}{2} = s_b\left(1 + aT\right).$$

We have consequently proved that the two averages are equal (to a first order of approximation). Hence, our procedure of taking the average of an odd number of readings on one side and an even number on the other, and obtaining the mean of these two averages for our zero point is valid.

558. Residual Error Resulting from the Use of Stoichiometric Proportions in the Running of a Control. — In § 56 it was stated that the weight of the constituent being determined in an unknown sample can be calculated from the relationship,

$$\frac{\text{Result found for standard}}{\text{Result found in unknown}} = \frac{\text{Weight of constituent in standard}}{X}, \quad (1)$$

where X stands for the weight of constituent in the unknown sample. In order to show to what extent the determinate error is reduced by this procedure, let r be the determinate or constant error of the method. Let C be the weight of constituent in the standard substance, V the theoretical chemical equivalent corresponding to C; likewise let C' and V' have a similar significance in regard to the unknown substance. We then have

$$V + r = \text{result found for standard substance}$$
$$V' + r = \text{``\qquad``\qquad`` unknown\qquad``}$$

Substituting these expressions in equation (1), we get

$$\frac{V + r}{V' + r} = \frac{C}{X}, \quad (2)$$

which upon rearrangement gives

$$X = \frac{V' + r}{V + r}C. \quad (3)$$

Now from the law of chemical equivalence we have that $C = kV$ and $C' = kV'$, where k is the appropriate chemical factor. Hence $\frac{C'}{C} = \frac{V'}{V}$ or rearranging,

$$C' = \frac{V'}{V}C. \quad (4)$$

From a comparison of equations (3) and (4) it is seen that our problem is in reality to find out how much the ratio $\frac{V' + r}{V + r}$ differs from the ratio $\frac{V'}{V}$.

To show what this difference is let us expand the ratio $\dfrac{V' + r}{V + r}$ by actually carrying out the indicated division. We get

$$\frac{V' + r}{V + r} = \frac{V'}{V} + \frac{r}{V}\left(1 - \frac{V'}{V}\right) - \frac{r^2}{V^2}\left(1 - \frac{V'}{V}\right) + \ldots \tag{5}$$

This expansion is a convergent series and for the purposes in hand we may neglect its terms of a higher degree than the first since they contribute an amount which is negligible with respect to the first degree term. We thus obtain

$$\frac{V' + r}{V + r} = \frac{V'}{V} + \frac{r}{V}\left(1 - \frac{V'}{V}\right), \tag{6}$$

or since it is the difference between the ratio $\dfrac{V' + r}{V + r}$ and $\dfrac{V'}{V}$ that we are looking for, let us transpose the term $\dfrac{V'}{V}$ to the left-hand member, thus getting for our difference that

$$\frac{V' + r}{V + r} - \frac{V'}{V} = \frac{r}{V}\left(1 - \frac{V'}{V}\right). \tag{7}$$

Now if $V' = V$, this difference reduces at once to zero and we then have $\dfrac{V' + r}{V + r} = \dfrac{V'}{V}$. Under these circumstances the value of X as given by equation (3) will be the same as the value of C' as given by equation (4); from which we see that the use of equation (1) eliminates the determinate error when $V' = V$, or (since r is a constant quantity), when $V' + r = V + r$, or further, when $C' = C$.

If V' differs from V, the right-hand member of (7) does not reduce to zero and we then have that $\dfrac{V' + r}{V + r}$ is not the same as $\dfrac{V'}{V}$; from which it follows that X will be different from C'.

This difference between X and C', i.e., $X - C'$, is the amount by which X will be in error. In order to gain an idea of the magnitude of this difference, $X - C'$, let us find out in accordance with our definition for the measure of magnitude of a constant error, the ratio that it bears to C'; namely, let us investigate the ratio

$$\frac{X - C'}{C'}. \tag{8}$$

By subtracting equation (4) from (3) and remembering that $\dfrac{V' + r}{V + r} = \dfrac{V'}{V} + \dfrac{r}{V}\left(1 - \dfrac{V'}{V}\right)$, we get

$$X - C' = \frac{r}{V}\left(1 - \frac{V'}{V}\right)C.' \tag{9}$$

From equation (4) we have that $C' = \dfrac{V'}{V}C$, whence, dividing this equation into (9), member by member, we have

$$\frac{X - C'}{C'} = \frac{r}{V'}\left(1 - \frac{V'}{V}\right), \tag{10}$$

or changing the form of the right-hand member, we get

$$\frac{X - C'}{C'} = -\frac{r}{V}\left(1 - \frac{V}{V'}\right). \tag{11}$$

By assigning values to $\frac{r}{V}$ and $\frac{V}{V'}$ we are able to get numerical values for the ratio $\frac{X - C'}{C'}$, which values of course are a measure of the magnitude of the error in X. The values which have been thus obtained have been given in Table 7 of § 56.

559. Nernst's Formula for Electrode Potentials. — There are three forms of this very important formula which give, respectively, the potential difference between

1. A metal and its ions

$$e = \frac{0.0001987T}{n} \log \frac{[\mathrm{Cu^{++}}]}{K_{\mathrm{Cu^{++}, Cu}}}$$

2. Simple ions of a metal and its ions of a lower valence

$$e = \frac{0.0001987T}{n} \log \frac{[\mathrm{Fe^{+++}}]}{[\mathrm{Fe^{++}}] \times K_{\mathrm{Fe^{+++}, Fe^{++}}}}$$

3. Complex ions of a metal and its ions of lower valence

$$e = \frac{0.0001987T}{n} \log \frac{[\mathrm{MnO_4^-}][\mathrm{H^+}]^8}{[\mathrm{Mn^{++}}] \times K_{\mathrm{MnO_4^-, Mn^{++}}}}$$

where e is the potential difference in volts, n the change of charge in going from one state of oxidation to the other, T the absolute temperature, and K a characteristic constant. We shall develop only the first form of the formula, and refer the student to text books on Physical Chemistry for the derivation of the second and third forms.

Before taking up this derivation in detail, it will be advantageous to present the following survey of the steps of the logic employed.

A. We suppose a rod of metal to be partially immersed in a solution of its ions and equilibrium to have been established between the metal and its ions.

B. We next imagine the system to undergo an infinitesimal virtual displacement from its equilibrium condition by the passage of a very small quantity of metal, say dm moles, from the elemental to the ionic state.

C. We then calculate the separate amounts of work done in accordance with the virtual displacement and put their sum, equal to zero, taking account of the signs of the work. It is a property of a virtual displacement that the sum of the work·elements is equal to zero.

D. We solve for e the equation obtained from C after reducing our work units to the same standard unit for consistency, choosing as our standard unit the joule (volt-coulomb).

E. We then determine the value of the characteristic constant K.

Derivation

A. Suppose a rod of metal to be partially immersed in a solution of its ions. By virtue of its solution tension P it tends to go into solution in the film of solution bathing the metal, as positively charged ions, leaving the metal negatively charged. Thus there results the formation of a double layer, known as the Helmholtz Double Layer of negative charges on the metal and positive charges on the ions. Between the negative and the positive charges there is an electrostatic attraction, which we shall designate by e and which, in reality, is the potential in which we are interested.
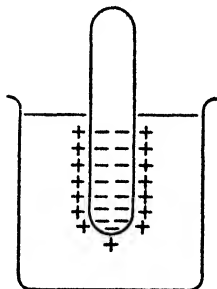
The process of solution continues until equilibrium is established between the following forces:

Fig. 132.

a. Solution tension P tending to force the metal into solution.

b. Electrostatic attraction e tending to draw the ions back to the metal.

c. Osmotic pressure p tending to force ions out of solution.

Thus we have,

Solution Tension = Electrostatic Attraction + Osmotic Pressure

B. Suppose the following virtual displacement: dm moles of metal pass from the elemental to the ionic state; along with this passage there will be transferred $96,500 \times n \times dm$ coulombs of electricity where n represents the valence of the ion.

C. To calculate the separate amounts of work involved we change the form of our equilibrium equation by bringing the Osmotic Pressure to the left-hand side, thus,

Solution Tension − Osmotic Pressure = Electrostatic Attraction

Allows calculation of Osmotic Work   Allows calculation of Electric Work

The amount of osmotic work is arrived at as follows: The transfer of 1 mole of substance from the osmotic pressure P to p at constant temperature T requires a decrease of free energy equal to

$$\int_P^p V \, dp.$$

If we accept as the equation for osmotic pressure

$$pV = RT$$

we have

$$\int_P^p V \, dp = RT \int_P^p \frac{dp}{p} = RT \ln p \Big|_P^p = RT \ln \frac{p}{P}.$$

[683]

We will consider that the system does the work as far as the osmotic work is concerned, so that the sign of the work will be positive. For dm moles the osmotic work will be

$$RT \ln \frac{p}{P} \times dm.$$

The amount of electrical work corresponds to the transfer of ($96,500 \times n \times dm$) coulombs at the potential e, or if we express e in volts it is

$$(96,500 \times n \times dm \times e) \text{ volt-coulombs.}$$

We will consider that the system has this amount of work done upon it so that the sign will be negative, or,

$$- (96,500 \times n \times dm \times e) \text{ volt-coulombs.}$$

Finally, remembering that 1 volt-coulomb = 1 joule, and substituting 1.98×4.184 or 8.31 joules/°C for R we have,

$$- (96,500 \times n \times dm \times e) \text{ joules} + 8.31\, T \ln \frac{p}{P} \text{ joules} = 0.$$

$D.$ Solving for e we get,

$$-e = -\frac{8.31\, T}{n \times 96,500} \ln \frac{p}{P}$$

and

$$e = \frac{8.31\, T}{n \times 96,500} \ln \frac{p}{P}$$

or transforming from natural logs to ordinary logs, by multiplying by the modulus 2.308,

$$e = \frac{8.31\, T \times 2.308}{n \times 96,500} \log \frac{p}{P}$$

or

$$e = \frac{0.000198\, T}{n} \log \frac{p}{P}.$$

To express our logarithmic ratio in terms of the activity of the ion, a_{ion}, and a characteristic constant, K, we note that osmotic pressure is proportional to the activity and that the solution tension is a constant for any given temperature; whence we get

$$e = \frac{0.000198\, T}{n} \log \frac{k \times a_{\text{ion}}}{K'}.$$

We can combine the two constants into one, giving finally

$$e = \frac{0.000198\, T}{n} \log \frac{a_{\text{ion}}}{K}.$$

In cases where the salt effect is considered negligible, we may use the ion concentration c_{ion} in place of the ion activity a_{ion} and, hence,

$$e = \frac{0.000198\, T}{n} \log \frac{c_{\text{ion}}}{K}$$

$E.$ We note that in our final equation there are two unknowns, e and K, and, hence, if we can determine the value of one, it fixes the value of the other.

Unfortunately, there is at present no direct experimental method of measuring either e or the solution tension, P, upon which K depends. Hence, we resort to the device of assigning an arbitrary value of zero to the potential at 25° between H^+ having an activity of 1, and H_2 furnished at one atmosphere. This gives for the hydrogen ion-hydrogen system

$$0 = \frac{0.000198\,T}{1} \log \frac{1}{K_{H^+,\ H_2}}$$

which upon being solved for $K_{H^+,\ H_2}$ gives $K_{H^+,\ H_2} = 1$. As pointed out in § 304 the activity of H^+ is 1 in a 1.2 M solution of HCl.

For other systems we can construct an electromotive force combination using a hydrogen half-cell thus,

(Pt) H_2 (1 atmosphere) | H^+ (activity = 1) |
                    Saturated KCl | Cu^{++} (activity = 0.1) | Cu^{++}
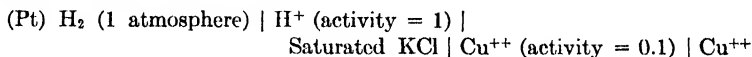
The observed voltage E of this combination at 25° is $+ 0.34$ volts, the Cu pole being the positive pole. Now

$$E = e_{Cu^{++},\ Cu} - e_{H^+,\ H_2}$$

whence

$$e_{Cu^{++},\ Cu} = + 0.310 \text{ volts.}$$

Substituting, in the Nernst equation we get

$$+ 0.34 = \frac{0.000198(273 + 25)}{2} \log \frac{1 \times 10^{-1}}{K_{Cu^{++},\ Cu}}$$

and solving for $K_{Cu^{++},\ Cu}$ we obtain

$$K_{Cu^{++},\ Cu} = 3 \times 10^{-12}.$$

560. Tristimulus Values. -- It had been established by the work of Maxwell (1854), Konig and Dieterici (1892), and Abney (1913), (see Report of Colorimetry Committee of the Optical Society of America, 1922) that any color can be matched (as observed by a normal observer) by definite proportions of three spectrum colors the wave lengths of which are respectively near the two ends and the middle of the visible spectrum. A spectrum color of such a choice is variously referred to as a *primary* or fundamental stimulus, or an additive, fundamental, or physiological primary. The definite proportions of the three primaries required to match a given color are called the *tristimulus values.*

About the year 1928 Wright and Guild in England, each working independently, re-determined the tristimulus values for the spectrum colors in terms of the set of primaries that each had adopted. Each investigator employed a number of very carefully selected observers. Wright in his investigation used, as primaries, spectrum colors the wave lengths of which were 460 mμ (blue), 530 mμ (green) and 650 mμ (red). Guild in his work used primaries which were produced by means of blue, green and red filters. Their tristimulus values were different, however, since they had not employed the same primaries. Nevertheless this difference is immaterial in a certain sense because the

tristimulus values are employed merely as intermediates in terms of which two colors can be compared.

Interrelation of Tristimulus Values. — There is a real drawback to either set of tristimulus values of Wright or Guild, or to any set of tristimulus values determined by the use of real primaries, in that no set of real primaries can be found that will match all colors including the spectrum colors without employing negative amounts of at least one of the primaries. By a negative amount is meant that the primary is transferred to the opposite side of the field where it is combined with the radiation the tristimulus values of which are being determined. This occurrence of negative amounts of primaries complicates the use of a triangular diagram for specifying the tristimulus values of a color.

It is possible, however, to avoid the use of negative amounts of primaries in the specification of a color by using, as triangular coördinates, primaries that lie outside the realm of real colors. This result is accomplished as follows: For real colors, the tristimulus values which apply to one set of primaries can be converted to tristimulus values which apply to another set of primaries by making use of the linear transformation:

$$r_1 = k_1 r + k_2 g + k_3 b$$
$$g_1 = k_4 r + k_5 g + k_6 b$$
$$b_1 = k_7 r + k_8 g + k_9 b$$

where r, g, and b are tristimulus values based on one set of primaries, r_1, g_1, b_1 are tristimulus values based on the new set of primaries, and k_1, k_2, ... k_8, k_9 are the tristimulus values of the original primaries on the basis of the new primaries.

I. C. I. Tristimulus Values. — By an extension of the above idea the International Committee on Illumination in 1931 adopted a set of tristimulus values derived from the data of Wright and of Guild in which the primaries X, Y, and Z lie outside the realm of real colors. These values are given for selected intervals in the following table and shown graphically in Figure 130.

I. C. I. TRISTIMULUS VALUES

Wave Length mμ	X	Y	Z
400	0.0143	0.0004	0.0679
450	.3362	0.0380	1.7721
500	.0049	.3230	.2720
550	.4334	.9950	.0087
600	1.0622	.6310	.0008
650	.2835	.1070	.0000
700	.0114	.0041	.0000

The values indicate the amount of each of the I. C. I. primaries required to match the color of a unit quantity of radiant energy of the various wave lengths.

Plotting the Chromaticity of a Color. — Let us suppose that the chromaticity of a color corresponds to X, Y, and Z units. We may also express this same composition in terms of the fractional ratio that each component bears to the sum of all three components, namely:

$$x = \frac{X}{X + Y + Z}$$

$$y = \frac{Y}{X + Y + Z}$$

$$z = \frac{Z}{X + Y + Z}.$$

The quantities x, y, z are called trichromatic coefficients or trichromatic coördinates.[16] It is to be noted that only two of them are independent, since

$$x + y + z = 1.$$

Fig. 130

I. C. I. Tristimulus Values

By virtue of this fact, we are able to plot chromaticity on a two-dimensional diagram, employing, preferably, the y coefficient as ordinate and the x coefficient as abscissa; this selection gives the graph of Figure 131. The neutral or gray point corresponds to $x = \frac{1}{3}$, $y = \frac{1}{3}$; illuminant C is represented by the point C. Pure colors lie on the spectrum locus; other colors lie inside the enclosed area. The diagram does not give the brightness of the color, but this is directly ascertainable from the value of the Y primary, since this has been so chosen that its value, multiplied by 100, gives the brightness.

[16] These expressions suggest those used by the chemist for expressing composition in terms of mole fractions. Let the composition of a solution be N_1 moles of A, N_2 moles of B and N_3 moles of C; then the corresponding mole fractions of A, B and C are:

$$n_1 = \frac{N_1}{N_1 + N_2 + N_3}$$

$$n_2 = \frac{N_2}{N_1 + N_2 + N_3}$$

$$n_3 = \frac{N_3}{N_1 + N_2 + N_3}$$

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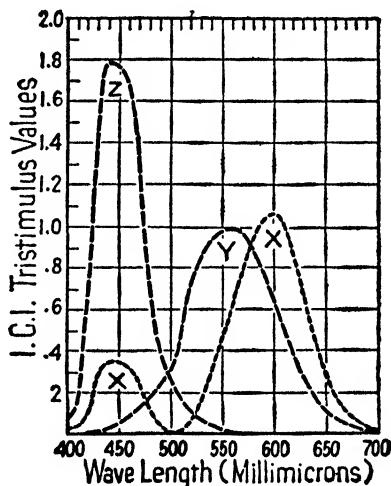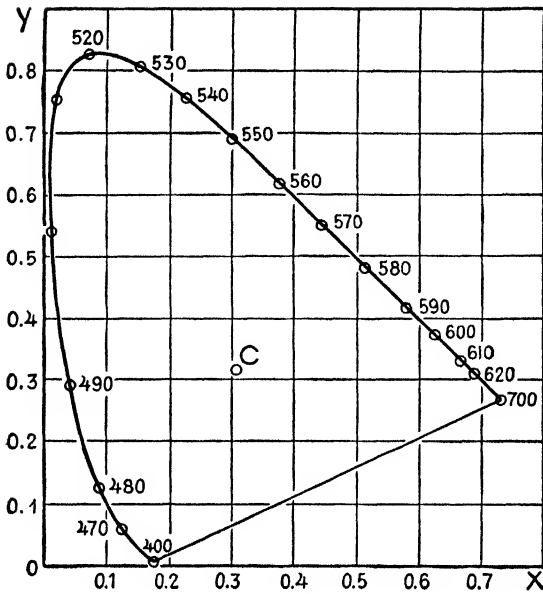
Fig. 131

Chromaticity Diagram with Trichromatic Coördinates x and y

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