ELEMENTARY QUANTITATIVE ANALYSIS
Theory and Practice

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PREFACE

Thanks to the kind reception that previous editions of this work has received from colleagues and students, and the helpful and constructive suggestions that have been received from many of them, the authors have undertaken their most thorough and complete revision of the project since its inception in a preliminary lithoprinted form.

The book has been taken back to manuscript form, and although the content necessarily remains approximately the same, there have been many slight, but it is hoped, useful changes in arrangement in a number of chapters. The more significant changes and the nature of the new material which has been introduced are explained briefly in the following paragraphs.

The literature summary has been transferred to the Appendix, as have sections on the use of logarithms, exponential expressions, and the solution of quadratic equations.

The introduction to the laboratory work has been moved ahead to the second chapter which follows a very brief introductory one. An attempt has been made to include in the second chapter all of those operations that are apt to be required in both volumetric and gravimetric procedures. A special introduction to gravimetric analysis in Chapter XV precedes the simple gravimetric determinations.

The balance, weighing and related matters form such an extensive body of material that the third chapter is devoted to these topics. A newly organized chapter entitled Scientific Measurements deals with accuracy, precision, errors, etc

Subsequent to the fifth chapter, which contains a revised treatment of fundamental laws and theories, are Chapters VI to XIV, inclusive, which deal with volumetric analysis in substantially the same order and scope of treatment as in previous editions. Many minor revisions have been made. More significant changes are a thorough revision of the chapter on the Theory of Neutralization, a rearrangement and modification of the chapter on the Theory of Oxidation Reduction Methods, with introduction of fresh material toward the end of the chapter relative to oxidation-reduction levels (E_0 values) as a function of acidity and other factors. A procedure for the Kjehldahl digestion method for Nitrogen has been added to the Procedures in the field of Acidimetry and Alkalimetry. An important modification has been made in the methyl orange method for examination of soda ash, based upon researches at the University of Michigan. Separate chapters are now devoted to Oxidations with Potassium Bichromate and with Ceric Sulfate, respectively.

In the gravimetric field procedures for phosphorus in phosphate rock and for the precipitation of zinc sulfide have been added. The chapters on Gravimetric Analysis, XV, and Simple Determinations, XVI, are followed by a revised chapter on Quantitative Separations, XVII, which is followed by the chapter on Gravimetric Separations.

The order of treatment of the Theory of Electrolytic Precipitations, XIX, has been considerably modified and numerous changes have been made. The practical chapter, XX, on Analysis of Alloys has few changes. New work of the National Bureau of Standards on the effect of a trace of chloride upon deposition of copper has been included.

A new chapter on Colorimetry, XXI, concludes the text. Mention of transfer of the literature summary and explanation of the use of logarithms to the Appendix has been made. The most significant change in the Appendix is the insertion of a five-place logarithm table instead of the four-place one.

Some general features of the revision that are of interest are: The addition of a substantial number of new or revised illustrations; the inclusion of different problems in place of those of the previous edition in nearly every set, and the inclusion of answers to a substantial portion of the problems in almost every set.

The authors make grateful acknowledgment to Professor K. Fajans of the University of Michigan who reviewed the theory and practice of the use of adsorption indicators in Chapter IX, and made detailed suggestions which have been used; also to Professor A. L. Ferguson of the University of Michigan who made many constructive suggestions which have been used in the revision of the chapter on the Theory of Electrodeposition. The further helpful criticism and suggestions of Professor E. R. Caley are gratefully acknowledged.

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May, 1940. N. HOWELL FURMAN.

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ELEMENTARY QUANTITATIVE ANALYSIS

CHAPTER I

INTRODUCTION

Analytical Chemistry. The analytical branch of chemistry deals with the theory and practice of the detection and the quantitative estimation of the substances that are present in compounds or mixtures. *Qualitative analysis* has for its primary goal the detection of the various substances that may be present in a given specimen of material; a good qualitative analytical scheme, if properly employed, is capable of giving much valuable information about the relative proportions of the substances that are present. A rough knowledge of these proportions is of great value in making a choice between alternative quantitative methods. *Quantitative analysis* is concerned with the determination of the amounts by weight or by volume of the various substances [1] in a known weight or volume of a compound or a mixture. The results of the analysis are usually expressed in percentages of the substances that are present.

In an *ultimate analysis* the percentages of the elements in the substance are found. For example, the determination of carbon, hydrogen and oxygen in an organic substance or of copper, sulfur and oxygen in a compound is an ultimate analysis. A *proximate analysis* is the determination of certain groups of substances. Illustrations are the determination of insoluble matter, or of volatile matter; the insoluble matter from limestone after treatment with acid of definite concentration may

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[1] The rather vague phrase "various substances" has been used in order to make the definitions sufficiently broad. At present instruction in analysis is limited to the detection and the estimation of elements, ions, radicals and compounds, the last by microscopic or x-ray technique. The rapid progress in the separation of isotopes has made methods for their estimation of considerable importance in research work. Mass spectrographic and other physico-chemical methods have been utilized.

consist of silica, clay and feldspar. Volatile matter will include moisture and all other substances that escape at the temperature in question. An analysis may be *partial* or *complete;* the latter may include the estimation of all of the substances that can be detected by the most sensitive methods; frequently a complete analysis includes only those substances that are detected in the ordinary qualitative analysis of a suitable sample which is often from 0.5 to 1 g. in weight; much larger samples are used when traces of substances are to be estimated.

The Scope of the Subject. A preliminary course in quantitative analysis is usually designed as an introduction to the theory and to certain types of manipulation. The latter are selected with a view toward correlation with other courses and toward the interests of a diversified group including premedical, engineering and chemical students as well as others not intending to use the subject professionally. The emphasis is frequently upon the subject as an introduction to the principles of scientific research rather than upon its practical utility in any limited field. The laboratory procedures usually deal with inorganic substances; the quantitative examination of organic substances is more commonly dealt with in advanced or special courses after a suitable background of organic chemistry has been acquired.

Although analytical chemistry is one of the older branches of the subject, its methods are by no means static or fixed. Further research by especially trained scientists is necessary in this field as well as in all others for the progress of science and civilization. Thousands of individuals in the laboratories of various universities, public or private research foundations and industries are engaged primarily in developing new or improved methods of chemical analysis. The results of such researches are to be found in papers in various scientific journals, text and reference works and special treatises. A brief guide to the special literature of analytical chemistry is given in the Appendix.

A Classification of Analytical Methods.[1] A distinction will be made between two principal classes of methods: I. Those in

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[1] A more detailed and perhaps more logical classification has been evolved by M. G. Mellon and D. R. Mellon, J. Chem. Education **14**, **365** (**1937**).

which the final measurement of the substance sought is by direct or indirect measurement of the weight, volume or area of the substance in a measured quantity of the original material. II. Those methods in which the final measurement is of some physical property of the system as a whole, e.g., color, electrical conductance, etc. This group of methods will be designated as *physico-chemical;* certain writers classify them as *instrumental methods* of analysis because some special instrument such as a colorimeter, spectrograph, potentiometer, etc., is usually necessary for the proper application of the method.

In the first group belong the two principal methods that are practiced in general, namely *gravimetric* and *volumetric* or titration methods, and these comprise the main substance of most elementary courses. *Gas analysis* and certain other methods also fall into this general group.

Gravimetric analysis consists in measuring the sample of the original substance and isolating and weighing an element or one of its stable compounds. For example, a weighed portion of an alloy of copper and nickel may be dissolved in nitric acid and the copper deposited electrolytically from the solution upon a weighed platinum foil. The gain in weight of the foil represents the copper deposited, since nickel is not deposited from an acidified solution under the conditions of electrolysis.

In the majority of analyses it is not practical to isolate the various elements because of their reactivity. In general it is better to transform each element completely into one of its stable compounds and to determine the weight of the latter. The weight of the element in question is then calculated from the weight of the pure compound. For example, magnesium is very frequently precipitated as the crystalline double phosphate, $MgNH_4PO_4 \cdot 6H_2O$. Upon careful washing, drying and heating at a proper temperature the pyrophosphate, $Mg_2P_2O_7$, is formed: $2MgNH_4PO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O$. The weight of the magnesium is calculated from the weight of the pyrophosphate:

$$Mg_2P_2O_7 : 2Mg$$
$$\text{Mol. wt.} : 2 \times \text{at. wt.} = \text{wt. of pyrophosphate} : x$$
$$x = \text{wt. of magnesium found.}$$

Volumetric analysis consists in measuring the amount of a solution of accurately known concentration that reacts quantitatively with some particular substance in the solution of a weighed or otherwise measured portion of the original substance. The weight of the substance sought is thus found indirectly from the amount of the known (standard) solution that is required. It is necessary to have some means of detecting the completion or *end-point* of the volumetric reaction, that is, an *indicator.* The process of finding the amount of standard solution is called a *titration.* Illustration.—Ammonium thiocyanate, NH_4CNS, precipitates silver quantitatively as silver thiocyanate, AgCNS. If ferric ion is present the first slight excess (one drop or less) of the thiocyanate solution beyond that required by the silver gives a pale reddish-brown coloration due to the formation of complex ferric thiocyanate.

Gravimetric and volumetric procedures are stressed in introductory courses because the principles and the manipulation are essential in other courses in chemistry and in a wide variety of types of investigation. A knowledge of these methods is also essential in connection with most of the physico-chemical methods. The following classification will give some idea as to the nature of the various types of methods.

QUANTITATIVE ANALYTICAL METHODS

I. **Methods in Which the Weight or Volume of the Substance Sought Is Measured Directly or Indirectly.**

A. **Gravimetric Methods.**

(1) The substance sought is precipitated chemically.

(2) Electroanalysis. The substance sought is precipitated by electrolysis.

(3) Evolution of Gases. The gas or vapor may be absorbed and determined by the gain in weight of the absorption vessel.
Alternatively, the loss in weight of the original substance may be determined.

B. **Volumetric or Titration Methods.** The completion of the reaction is shown:

(1) By an indicator of chemical nature.

(2) Physico-chemically

(a) By change in electrical conductance of the solution, or Conductometric Titration.

(b) By changes in potential of suitable electrodes, i.e., Potentiometric Titration.

(c) By other physical measurements, e.g., temperature rise; change in refractivity, etc.

In general method (1) is the most convenient and useful.

C. **Gas Analysis.** The individual components of a measured volume are removed successively by absorption, combustion or condensation. The residual volume is measured after removal of each. Temperature and pressure are either kept constant, or changes are taken into account.

D. **Other Methods.** Volumes of liquids or solids may be read after separation by centrifuging from various mixtures. Liquids may be distilled with an immiscible liquid and the volume read. This method is used very frequently for moisture which is distilled out and collected under xylene, toluene, etc., or above a heavier liquid such as tetrachlorethane which is often used as a distilling solvent.

Measurement of area, or diameter in case of approximately spherical particles under the microscope is used in mineral analysis and for other purposes. The weight of any particular substance is estimated from the volume and density. Indirect determination of weight by measurement of area has been proposed for precipitates in contact with the solution. The process, termed "areametric analysis" has to be standardized with known amounts of the substance in question.[1]

II. **Methods in Which the Final Measurement Is Made upon the System as a Whole. Physico-chemical Methods.** Calibration Data Are Necessary.

A. **Mechanical.**

Specific gravity measurement serves as the basis of many analyses, especially of binary mixtures of liquids, e.g., alcohol and water. Certain alloys may be analyzed fairly accurately by a single specific gravity determination.

B. **Thermal.**

Transition points, especially melting points, are used to obtain analytical information as to purity of substances or composition of binary mixtures. Thermal conductance serves as a basis of gas analyses.

C. **Electrical.**

Conductance, electromotive force, magnetic susceptibility and dielectric constant measurements may be used in order to determine composition from a single measurement for many systems.

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[1] V. Damerell et al., Areametric Analysis, J. Am. Chem. Soc. **57**, 2725 (1935); Ind. Eng. Chem. Anal. Ed. **9**, 123 (137).

D. Optical.

(1) *Emission of spectra.*
The substance is caused to emit radiation by a flame, a high frequency spark or an arc. The spectrum is photographed and line intensities are measured. A grating spectrograph or one with quartz prism and lenses is essential for most work. The method is much used in the analysis of metals and alloys, minerals, ash of plants, etc.

(2) *Absorption of radiation.*

(a) *Colorimetry.* Unfiltered light is allowed to traverse the unknown and the standard and the intensities of the transmitted beams are matched, most commonly by changing the depth of liquid traversed. Fluorescent effects are used in a similar fashion. The source in this case is usually a mercury vapor lamp.

(b) *Spectrophotometry.* An approximately monochromatic spectral region is observed with the aid of filters or a prism. The percentage of transmission is measured, for the substance analyzed as compared with the solvent, or a standard.

(3) *Diffraction.*
X-rays are diffracted by the atoms of a solid. The photographed diffraction pattern of crystalline substances serves as a basis both of qualitative and quantitative estimations.

(4) *Reflection and diffraction.*
Nephelometry is based upon the observation of the light scattered by a suspension in a direction at right angles to the incident light. The method is extremely useful in estimating small amounts of suspended solids. The nephelometer has long been a fundamental tool in atomic weight investigations.

(5) *Refraction.*

(a) *Refractometry.* The measurement of refractive index is a useful test of the purity of many oils, fats and waxes. The refractive index of many binary mixtures changes in linear fashion with concentration over a considerable range. The refractive index is an important property of a crystal.

(b) *Interferometry.* This process is based on a differential refractive principle. Interference fringes due to differences in optical path for the unknown and the standard form the basis of observation. The device is useful in the analysis of gases, solutions such as sea-water, liquid mixtures, etc.

(6) *Optical rotation.*
Rotation of the plane of polarization of plane-polarized light from a monochromatic source is especially useful in the analysis of solutions of sugars. The method applies to optically active substances or to substances which modify the activity of such substances. For example, tartrates of iron and aluminum investigated through the optical activity changes that occur when the complexes have been formed.

E. **Sonic effects.**
The interference of sound waves in gaseous mixtures may be observed with precision. For certain types of mixtures this property varies in a sensitive and definite fashion with change in composition of the mixture. The instrument is called a sonic interferometer.

The application of the majority of the physico-chemical methods requires a previous calibration of the instrument with known mixtures that have been analyzed by gravimetric, volumetric or gas analytical methods. When the calibration data have been established, the physico-chemical methods enable one to make many similar analyses with great speed and frequently with very high precision. For example, traces of elements in purified metals like zinc, magnesium or copper may be estimated spectrographically with an ease and precision that is scarcely obtainable by other methods. This particular method involves a very considerable capital investment, a preliminary investigation of each application, and its value is greatest when a very large number of similar specimens are to be analyzed within a brief interval of time.

The majority of the simpler texts and reference books describe principally the gravimetric and volumetric methods, with perhaps a brief account of a few of the physico-chemical methods, as for example, colorimetry. The more comprehensive reference books, special monographs and the journal literature should be consulted by those interested in any particular method. A selection of suitable sources is given in the Appendix.

Macro-, Semimicro- and Microanalysis. Three rather distinct scales of operation are in common practice in both qualitative and quantitative analysis. In quantitative analysis the operations are said to be on a macro scale when the samples of material to be analyzed are of the order of grams, as for example 0.2 g. to 2. g. or more. There is no sharp division between macro- and semimicroanalysis, or between semimicro- and microanalysis. Semimicro samples are of the order of centigrams, commonly from 5 to 8 cg. (0.05-0.08 g.). Microanalysis usually deals with samples ranging from about 15 mg. down to 1 mg. or even less. This last field is a very popular and important one.[1] It requires a balance sufficiently sensitive,[2] and apparatus of small size and properly designed for this field of work. In the hands of a skilled operator the microtechnique saves much time, especially in the analysis of organic substances; its use is by no means limited to the organic field. Microanalysis is indispensable when only small quantities of rare or expensive substances are available for analysis.

The General Operations of Quantitative Analysis. In the complete examination of a material of unknown composition the following operations may be required:

1. *Sampling.* The material that is analyzed must be truly representative of the average composition of the substance in question. The selection of a representative sample of material in bulk is a difficult special problem that is fully as important as the analysis itself. A further discussion, with references, will be found in Chapter II.
2. *Preliminary Examination.* As much information as possible should be obtained from the appearance, hardness and other superficial characteristics of the substance. The use of a lens, microscope, magnet, knife, porcelain streak-plate, touchstone for precious metals, or other devices is often helpful.
3. *Division of the Sample.* Small fragments of material are reduced further in mortars of hardened steel or of agate. Soft materials may be ground in porcelain mortars. Substances that are very resistant to chemical attack must be ground in a suitable mill to pass a screen of 200 mesh (per sq. in.). Division to 80–100 mesh is often required.
4. *Qualitative Chemical Examination.*
5. *Drying at 100°–105° C.* to remove superficial moisture, for the majority of substances. Alloys do not need to be dried unless they have been treated with solvents to extract oil. Some substances are tested for moisture when received and again before analysis if necessary. In

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[1] F. Pregl, Quantitative Organic Microanalysis, 2nd Ed. Transl. by E. Fyleman, Blakiston, 1930; Niederl, J. B. and V. Niederl, Micromethods of Quantitative Organic Analysis, John Wiley & Sons, Inc., New York, 1938; L. T. Hallett, Quantitative Microchemical Analysis, pp. 2460–2547, Vol. II, Scott's Standard Methods of Chemical Analysis, D. Van Nostrand Co., New York, 1939.

[2] A. A. Benedetti-Pichler, Ind. Eng. Chem. Anal. Ed. **11**, 226 (1939). The use of standard types of balances for microanalysis is described.

some instances moisture at 100°–105° C. is found, and then combined water by heating to a definite higher temperature.

6. *Weighing.*
7. *Solution of Weighed Samples in an Appropriate Solvent.*

Gravimetric Analysis	**Volumetric Analysis**
8. *Preliminary Treatment:* Oxidation, reduction, removal of interfering substances, evaporation, etc.	8. *Preliminary Treatment:* Oxidation, reduction, etc.
9. *Precipitation.*	9. *Titration.*
10. *Filtration and Washing.*	10. *Calculation of Per Cent of Substance Found.*
11. *Test for Completeness of Precipitation.*	
12. *Drying and Final Heat Treatment.*	
13. *Cooling and Weighing.* (Heat treatments and weighings are repeated until constant weight is attained.)	
14. *Calculation of Per Cent of Substance Found.*	

It is evident that when standard solutions are available less time will be required for volumetric than for gravimetric analyses because of the time-consuming nature of precipitations, filtrations, heatings and weighings. Volumetric processes are not very specific and hence qualitative or quantitative tests have to be made in order to be sure that a single substance is being titrated. A very decided advantage of gravimetric methods is that the substance sought may be observed and tested qualitatively or quantitatively for purity; further purification may be undertaken or corrections may be determined on the basis of the tests.

In order to save time in elementary courses it is customary to have material available that has been properly sampled and divided so that the student may begin with the drying of the sample (fifth operation); or with the weighing in certain instances. If only solutions are issued for analysis much time may be saved, but valuable experience in the preliminary operations is lost.

CHAPTER II

INTRODUCTION TO LABORATORY WORK

THE GENERAL OPERATIONS OF QUANTITATIVE ANALYSIS

A series of properly conducted quantitative determinations is a logical introduction to more elaborate scientific investigations. For this and other reasons the subject is included in several curricula other than those of chemistry and chemical engineering. Success in this field as in others calls for a definite amount of *preliminary reading* and *planning,* the proper preparation of materials and apparatus, the taking of observations and the interpretation of the results. The qualities of *honesty* and *patience are vital;* given these one can develop suitable technique. Care, organization and neatness are essential; apparatus should be put away clean, and arranged so that special items can be found at once when needed. The desk and the balance and its surroundings and your share of the general equipment must be maintained in proper condition. Carelessness and sloppiness are incompatible with quantitative work, and may ruin not only the work of an individual, but of others as well.

The Notebook. One of the objectives of the course is training in the proper recording of scientific data. This involves the leaving of space for a table of contents or an index, the use of principal and sub-headings, dates, logical arrangement of observations and general neatness. The notation of the date when an observation is made together with the signature of the observer and a witness is routine practice in many industrial laboratories. In a course, the dating of observations has many valuable features for both student and teacher, for example in tracing the behavior of new or unstable substances that may be issued as unknowns. A permanently bound notebook is best; one about 5 × 7½ inches, opening at the side, is convenient for use at the balance. It is well to reserve a special part of the book for calculations; the left-hand page is frequently used for this purpose and for noting balance swings. *All weighings, burette readings* or other observations should be *neatly recorded* preferably in ink, *as soon as determined.* See p. 61 for the data that are essential in a typical case. The record should be so complete and well arranged that the data may be readily checked by an instructor. Determinations that are unsuccessful or apparently faulty should have a single diagonal line or an X drawn through them with a brief notation of the apparent difficulty. Sometimes such work will later be found to have been correct, but misinterpreted, or passable though not of high grade. The notebook is handed in with each report unless another system is in practice. Reports are to be made in the manner recommended; frequently special report forms are provided. The student is commonly judged on the basis of reports submitted. Frequently there is no penalty attached to a reasonable number of ineffective experiments; the emphasis is usually placed upon obtaining correct and concordant results within a reasonable period of time.

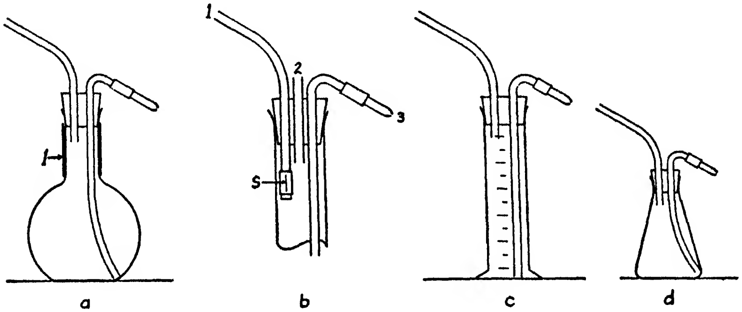

Fig. 1. Wash Bottles.

a. Common type; *1* indicates wrapping of twine or asbestos paper.
b. Bunsen valve at *s.* Upon closing the tube at *2* with a finger and blowing at *1* a stream of wash liquid will flow from tip *3* for some time.
c. A graduated cylinder used as a wash bottle; useful when a washing correction is to be made.
d. A small Erlenmeyer flask used as a wash bottle for special wash liquids.

Preliminary work. The desk equipment should be checked and arranged in an efficient fashion.

Wash bottles should be prepared for use. See Fig. 1. Usually a 1 liter and a 500 ml. flask are provided. It is convenient to have one of them, preferably the 500 ml. size, wrapped for use with hot wash liquids. Thin asbestos sheets, stout twine or other material as provided may be used.

The desiccators, Fig. 2, should be charged with fresh drying agent of suitable nature, as for example calcium chloride, calcium sulfate hemihydrate ("drierite"), anhydrous magnesium perchlorate ("dehydrite") or other desiccant. If the desiccator plate is free to slide, it should be wedged firmly with pieces of cork. The ground surface of the lid should be touched lightly with vaseline or stopcock lubricant at a few points, then rotated against the ground part of the main vessel. The use of too much grease will permit the lid to slide.

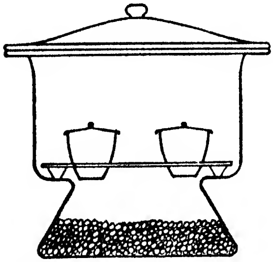

Fig. 2. Desiccator with Crucibles.

Stirring rods of various lengths should be available; they should be fire-polished or rounded at both ends after cutting to such lengths that about 2 cm. of the rod projects above the lip of the beaker or other vessel with which the rod is to be used. A short piece of stout glass rod flattened at one end is used by some workers to tamp down the asbestos in a Gooch crucible (see p. 30). Glass hooks may be needed to support cover glasses during evaporations and dryings. The hooks should be designed to fit any beaker or casserole. See Fig. 3. If cover glasses with ridges are provided the hooks will not be needed. Glass rods of proper diameter are rounded for use with rubber tips as "policemen."

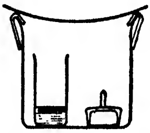

Fig. 3. Small Beaker; cover supported by glass hooks; weighing bottle.

Porcelain crucibles are marked for identification with letters or numbers. Ink or pencil that contains iron or other material that will fuse into the glaze of the crucible will be provided. The porcelain should be marked lightly to avoid blurring. After drying the crucible is gradually heated to redness, the crucible being supported as indicated on p. 32, Fig. 15; the flame is adjusted to give oxidizing conditions. If three or more similar crucibles are available it is convenient to make a rough preliminary weighing and to number them in order of increasing weight.

Reagents. The amounts of the various reagents that are used in individual determinations are in general small and the time required is important; therefore the rule is to avoid risk of contamination of reagents by return of material to a reagent bottle. Measure out the amount needed or a slight surplus, according to statements given in the procedures or as found by rough calculation. The stoppers that belong with the desk reagent bottles frequently have corresponding numbers; in any event see that no interchanges are made. The concentrated reagents and convenient dilute solutions prepared from them are as follows:

Concentrated Hydrochloric Acid, 12 N. ("C.P." conc. acid of sp. gr. 1.18-1.19).

Dilute Hydrochloric Acid, 6 N. Prepared by mixing the concentrated acid with an equal volume of water.

Concentrated Nitric Acid, 16 N. ("C.P." acid of sp. gr. about 1.42).

Dilute Nitric Acid, 6 N. Proportions: 38 ml. of the concentrated acid plus 62 ml. of water.

Concentrated Sulfuric Acid, 36 N. ("C.P." acid of sp. gr. 1.84 containing about 96 per cent of H_2SO_4 by weight.

Dilute Sulfuric Acid, 6 N. Prepared by pouring 1 volume of the concentrated acid slowly, with stirring, into 5 times its volume of water.

Concentrated Ammonium Hydroxide, 15 N. ("C.P." ammonium hydroxide of sp. gr. 0.90).

Dilute Ammonium Hydroxide, 6 N. Best prepared in small quantities immediately before use unless special containers with unattackable lining are available. Proportions: Two volumes of the concentrated reagent plus 3 volumes of water.

Silver Nitrate, 1 N. Supplied when needed in the work.

Water. In all quantitative procedures the water is to be the best grade of distilled water. It is assumed that all vessels have been cleaned, rinsed with tap water, and finally with distilled water. See "Cleaning of Apparatus," p. 15.

At times the procedures call for solutions of approximate strengths as for example 5 per cent sulfuric acid or 1 per cent nitric acid. By these are meant five and one per cent, respectively, of the concentrated acid. An alternative and perhaps better way of stating such concentrations is: Dilute sulfuric acid

(5 + 95) or dilute nitric acid (1 + 99), the first number in the parentheses always indicating the volume of the concentrated reagent that is added to the volume of water represented by the second figure. A graduated cylinder is used in making the measurements.

The preparation of a reagent of approximate *normality* from a stock solution of known specific gravity and composition is frequently necessary. Tables of specific gravity and the corresponding percentage compositions of various important solutions are to be found in the handbooks. See the Appendix.

Illustration. What volume of sulfuric acid of sp.gr. 1.84, containing 96.0 per cent by weight of H_2SO_4, will be needed to prepare 2 liters of the 6 N acid?

Two liters of 6 N acid contain $2 \times 6 \times \frac{98.1}{2} = 588.6$ g. of H_2SO_4. In 1 liter of the stock acid there are $1000 \times 1.84 \times \frac{96.0}{100} = 1766$ g. of H_2SO_4. Hence by proportion: $1766 : 1000 = 588.6 : x$. $x = 333$ ml. of the concentrated acid to be diluted to 2 liters.

If the normalities of the stock solutions are known the volume of the reagent to be used may be calculated more simply from the inverse volume—normality rule. See p. 141.

Every solution that is prepared should be made uniform by stirring, shaking or swirling it. Solutions of salts and of ammonia should be examined for insoluble matter derived from the container, stopper or other sources. As has been stated, it is wise to prepare the dilute ammonium hydroxide immediately before its use. Solutions of salts of approximate normalities are prepared by dissolving the proper amount of material that has been weighed on a platform balance provided for this purpose. The pan is protected with counterpoised glass, celluloid or paper, depending upon the nature of the material that is to be weighed. The solution is filtered if necessary (see p. 22).

Every effort is made to supply reagents of purity adequate for the work; frequent qualitative or "blank" tests are made to satisfy oneself that no errors are introduced from this source.

In critical work the following scheme is often used to estimate the effect of impurities in the reagents: one or more estimations are made, adding distilled water and reagents in the same amounts as would be used in the analysis; these solutions are subjected to all of the manipulations that are made in the analysis itself. This process is known as a *blank,* a *blank* on the *reagents, "running a blank," blank analysis,* etc. In this way an average correction for the reagents may be found, or one may be convinced that no error of significance is introduced by the reagents, filters, etc.

Due consideration must be given to the effect of the components of the air or of fumes from nearby operations that might affect work in progress. Material from the burner gases, filter paper, rods, policemen, etc., may cause errors which may be avoided by proper procedures. The rubber policemen are rinsed, letting the rinsings flow into the proper vessel, and removed before solutions are boiled. Rods are likewise rinsed down and removed prior to long boiling operations, or evaporation to dryness.

Unknowns for Analysis. Various systems are used for distributing substances to be analyzed, and proper attention should be given to the rules announced for their distribution. Most of the materials are to be dried for 2 hours at 100-105° C., and many of them may be dried over night in an electric oven. The substances should be obtained in advance so that no delay will result because of the time required for drying them. As soon as satisfactory results have been obtained in an analysis (see p. 70), they are reported in the manner announced.

The Cleaning of Apparatus. (a) *Glass and Porcelain.* The method of cleaning should be adapted to the substances that are to be removed. Water-soluble substances are simply washed out with hot or cold water, and the vessel is finally rinsed with successive small amounts of distilled water. The general rules for the solution of other materials should be considered in any particular case; see p. 20. For example ferric oxide, manganese dioxide and oxides in general are more apt to be removed by warm concentrated hydrochloric acid than by other solvents, notably chromic-sulfuric acid, which is a poor solvent in this case.

Volumetric glassware, especially burettes, may be thoroughly cleaned by a mixture containing the following: 30 g. sodium hydroxide, 4 g. sodium hexametaphosphate (trade name, Calgon), 8 g. trisodium phosphate and 1 liter water. A gram or two of sodium lauryl sulfate seems to improve its action in some cases. This solution should be used with a burette brush.

A persistent greasy layer or spot may be removed by acetone or by allowing a warm solution of sodium hydroxide, about 1 g. per 50 ml. of water, to stand in the vessel for 10-15 minutes; after rinsing with water, dilute hydrochloric acid, and water again, the vessel is usually clean. If not, the foregoing treatments may be repeated.

Chromic-sulfuric acid mixture. Concentrated sulfuric acid saturated with sodium bichromate, or with chromic acid added, has been much used for cleaning vessels. Due to its destructive action upon clothing and upon laboratory furniture, its use should be avoided when less corrosive or simpler agents will serve. The mixture may be used many times before becoming ineffective (indication?). It should be hot (80°-100° C.) but *not fuming or boiling* (about 240°-250° C.), and should be allowed to stand for 10-15 minutes in contact with the vessels to be cleaned. A large duriron evaporating dish is the best receptacle for this mixture. A set of beakers may be cleaned in one operation. The solution may be kept in the duriron dish if it is heated frequently to drive out water, otherwise it should, when cool, be returned to the storage bottle for further use. If any of the solution is spilled it must be cleaned up immediately. The vessels are rinsed thoroughly with tap water, then with small successive portions of distilled water.

Certain volumetric vessels may have been etched by alkali through careless previous handling. If thoroughly cleaned many of these vessels are capable of further service. An alkaline solution should not be stored in a calibrated flask, nor should it be left in a burette over night. Burettes with stopcocks unaffected by alkali are supplied by some manufacturers.

(b) *Platinum ware.* Although the first cost of platinum is high and its cost prohibitive for use in many beginning courses, the utensils if properly cleaned and cared for will give many years of service. Details of the care of platinum electrodes are given in Chapter XX. Platinum crucibles, when not in use should be kept in shape on forms of plastic materials or wood. They are cleaned by polishing with water and sea sand, or with scouring soap with a base of rounded sand or kieselguhr. Iron stains are best removed by placing in the crucible a gram or two of ammonium chloride and applying to the covered crucible the full flame of a Meker or similar burner for two or three minutes. Since platinum is attacked by hot alkalies, fused nitrates, fused cyanides, free metals, sulfides, sulfur, phosphorus and carbon at high temperatures, the foregoing substances and those from which they may be generated must not be heated in platinum. This means that all of the compounds of the easily reducible metals and metalloids should not be heated to a high temperature in platinum because reducing gases diffuse rapidly through the hot metal. Filter paper is burned off at the lowest possible temperature, and contact of the metal with the cone of unburned gas or with a luminous flame is avoided. Platinum vessels are used for fusions of silicates and other substances with sodium carbonate; or for heating silicates with a mixture of calcium carbonate and ammonium chloride. The removal of silica as silicon tetrafluoride is done in platinum; also the heating of silica, alumina (plus other refractory oxides), or of other difficultly reducible compounds. Double phosphates of ammonium and magnesium or other metals have been heated in platinum; occasionally reduction occurs and the crucible is damaged or ruined; this use of the crucible should be avoided. If alloying is suspected, the crucible is treated first with boiling dilute hydrochloric acid, followed by thorough washing, finally with distilled water; a similar treatment with dilute nitric acid is followed, and changes in weight and appearance are observed, and the acid extracts are tested, as a guide to other treatment. Fused potassium pyrosulfate dissolves many of the refractory oxides which are apt to adhere to some extent to platinum. It is best to consult reference books before attempting to carry out any unfamiliar process in platinum.

THE GENERAL OPERATIONS OF QUANTITATIVE ANALYSIS

1. **Sampling.** The sample that is selected for analysis must be made uniform and must properly represent the composition of the bulk of material from which it is taken; otherwise the time and effort spent in the analysis will be wasted. In small scale preparations of either inorganic or organic substances it is possible to make the whole preparation uniform, or to use the

quartering process (see below) and to grind a suitable portion of it.

Material in Bulk. The sampling of material in bulk as for example a shipload of ore, a train-load of fuel oil in separate cars, or of scrap metal, pigs of unrefined metal, etc., presents special problems which differ from case to case.[1] When possible a gross sample weighing several hundred pounds is taken by automatic sampling machinery at proper intervals during the unloading or loading of boats, cars, trucks, etc. This large sample is reduced to convenient bulk to transport to the laboratories of buyer, seller and referee analyst, either by mechanical methods or by piling and shoveling procedures, discarding alternate shovels in a definite way after thorough mixing, to form a long pile of definite shape and dimensions. Finally about 125 pounds of the material is ground, made into a well-mixed conical pile, and opposite quarters are rejected and the remainder again mixed to form a new conical pile which is again "quartered," etc. A representative sample weighing not more than a few pounds is finally sent to each of the laboratories concerned, and there ground and quartered further if necessary.

Metals. Pigs or other forms of metal are sampled by drilling or sawing at positions determined by considerations of probability and experience. Some metals, notably lead alloys, tin alloys, etc., have to be sampled while molten because of the segregation of certain components during the crystallization process. In mills where alloys are fabricated special test pieces are prepared from the stock material for physical and chemical tests.

In the procedures of the American Society for Testing Materials (see Appendix) there are included standard methods of sampling as well as analysis for important classes of substances that are dealt with in bulk.

The substances that are issued for analysis in a course are generally portions of well-mixed powders, properly subdivided alloys, or solutions. They are shaken well or otherwise mixed before weighing or measuring individual samples.

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[1] For a more detailed treatment of the problem, with further references, see J. B. Barnitt, "Standard Methods of Sampling," Vol. II, p. 1301, of Scott's Standard Methods of Chemical Analysis, 5th Ed., D. Van Nostrand Co., 1939.

2. **Preliminary Examination.** This is preliminary to the qualitative examination of a substance. It may involve mere visual inspection, or use of lens or microscope. Various implements such as knife, streak-plate, magnet, etc., are used. With an emery wheel certain ferro-alloys may be distinguished instantly by the appearance of the sparks. A full account of the methods of preliminary examination is to be found in the more extensive treatises on qualitative analysis.

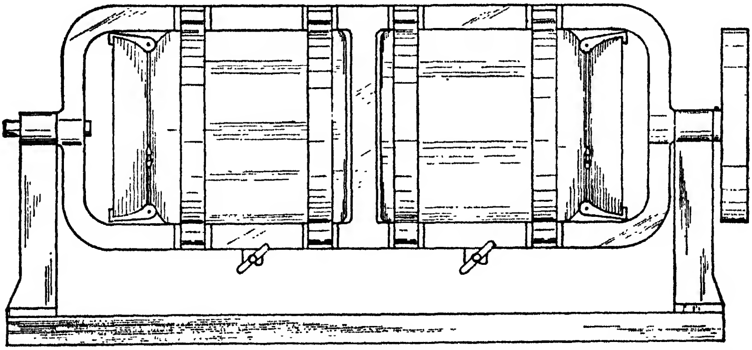

Fig. 4. A Ball Mill. The solids to be ground, together with flint balls are placed in the porcelain jars which are clamped in position as shown. The apparatus is rotated by motor (not shown) until the grinding has been completed (1–3 hours or longer).

3. **Subdivision of Materials.** The reduction of the gross sample has been discussed under "Sampling." If material is received in the laboratory in the form of small lumps, it is crushed in a mortar of suitable material or in a small motor-driven jaw-crusher, and ground to 100 mesh or finer in a ball-mill, Fig. 4, or other suitable grinder.

Small bits of hard material, for example mineral specimens, are crushed in a hardened steel mortar, the so-called diamond or Plattner mortar, Fig. 5. Final grinding is done in an agate mortar or one of hardened metal. Grinding may affect the composition of a material either by expelling water, promoting oxidation especially of ferrous to ferric oxide in minerals, or

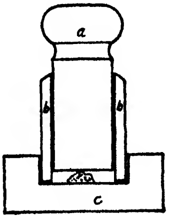

Fig. 5. Plattner or "Diamond" Mortar.

The piston *a* fits closely in the collar *b*. Upon hammering at *a* small lumps of materials may be powdered against the base *c*.

by abrading material from the mill or mortar. Data on these effects are given in Applied Inorganic Analysis, Hillebrand and Lundell, p. 669 ff.

4. **Qualitative Analysis.** This is performed by an adequate scheme which will include all of the elements that are apt to be present. In certain laboratories that have to do largely with metals and alloys and the ores from which they are derived the routine qualitative examination is made almost entirely with the aid of the spectrograph because of the speed and convenience of this technique.

5. **Drying.** Samples of solids, other than alloys, are dried at 100-105° C. unless instructions to the contrary are given. Two hours at this temperature is the minimum time for effective drying, and an over night heating is preferable in many cases. Unstable materials such as those containing a sulfide, an arsenite or an acid should be dried for not longer than two hours. The material that is to be dried is placed in a clean, dry weighing bottle, preferably of a wide form; the open bottle is placed in the smallest adequate beaker, and the latter is covered with a watch glass. Glass hooks may be used to raise the cover if this is thought desirable. Fig. 3, p. 12. In research work and in industrial routine operations many substances are encountered that must be dried at room temperature. This is done in a desiccator that can be evacuated through a side tube; the drying agent is chosen in view of the properties of the substance to be dried, and it may be acidic, basic or neutral, e.g., sulfuric acid; phosphorus pentoxide; fused potassium hydroxide; magnesium perchlorate.

6. **Weighing.** The balance, weighing and weights are discussed in Chapter III, p. 35.

7. **Solution of the Sample.** *Choice of Solvent.* Nitric acid attacks all of the common metals,—aluminum and chromium very slowly, due to protective films, except when these metals are alloyed with other metals. The concentrated acid does not attack iron. A solution is obtained in nearly all cases except with tin, which forms insoluble metastannic acid, and antimony. which forms a nearly insoluble mixture of antimonous and antimonic acids; precipitation of the latter is complete only when a greater amount of tin is present (coprecipitation by stannic acid). Concentrated hydrochloric acid dissolves all the

common metals except silver, mercury, bismuth, copper, arsenic and antimony. It dissolves lead slowly. Dilute sulfuric acid behaves much like hydrochloric acid but it does not attack lead. Boiling concentrated sulfuric acid attacks all the common metals and is a good solvent for mercury, bismuth, arsenic, antimony, tin and their alloys which are practically unattacked by the dilute acid. Hydrochloric acid containing nitric acid, or a chlorate, which liberates chlorine, attacks all the metals. The solvent action of hydrochloric acid or of dilute sulfuric acid, or of any other acid which reacts with the metals by the simple displacement of acid hydrogen without any side reactions, may be readily predicted by reference to the electromotive series. In this series the elements are arranged in the order in which they displace one another from the solutions of their salts, the more chemically active of the metals appearing at the top.

Electromotive Series. Metal.	*Standard Potential,*[1] *Volt.*
Li	—3.02
K	—2.92
Ba	—2.90
Sr	—2.89
Ca	—2.87
Na	—2.71
Mg	—2.34
Al	—1.67
Mn	—1.05
Zn	—0.762
Cr	—0.71
Fe	—0.44
Cd	—0.40
Co	—0.277
Ni	—0.25
Sn	—0.136
Pb	—0.126
H	0.000
Sb	0.212
As	0.247
Bi	0.32
Cu	0.344
Ag	0.799
Hg	0.799
Pt	1.2
Au	1.42

The electromotive series of the more common metals is shown. Hydrochloric acid dissolves all of metals above hydrogen in this series, but in the absence of air and other oxidizing agents it will not dissolve any of the metals below hydrogen. The solvent action of dilute sulfuric acid is the same, except that it will not dissolve lead, due to the formation of a surface film of lead sulfate.

Oxides are best dissolved by hydrochloric acid except in special cases where insoluble chlorides are formed. As a rule nitric acid is a very poor solvent for oxides, and nitrohydrochloric acid is inferior to hydrochloric acid.

All sulfides except mercuric sulfide are attacked by nitric

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[1] The numerical values for the standard potentials are those given by W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., 1938, and reproduced here with their permission. The convention regarding the sign is that used in Chapter XIX.

acid. Free sulfur is always formed, never hydrogen sulfide. The sulfides of silver, mercury, arsenic, copper, cobalt and nickel are practically insoluble in concentrated hydrochloric acid; hydrogen sulfide is liberated on treatment of the other sulfides with hydrochloric acid. Natural iron pyrites, FeS_2, is insoluble in hydrochloric acid, although ferrous sulfide, FeS, is easily soluble. Treatment with nitric and hydrochloric acids together oxidizes all sulfides to sulfur or to sulfuric acid, and under certain conditions entirely to the latter form.

Hot, 70 per cent perchloric acid, $HClO_4$, is a powerful oxidizing agent which attacks all the common metals and their sulfides. With tin and antimony insoluble acids are formed, but since all perchlorates are readily soluble, perchloric acid is often an excellent solvent. A certain amount of chloride is usually formed at the same time. Ignited chromic oxide which resists attack by other acids, is readily oxidized by hot concentrated perchloric acid to soluble chromic acid. *Contact of the hot vapor or of the hot concentrated acid with organic matter or with some easily oxidized inorganic substances may lead to dangerous explosions and is therefore avoided.* Dilute perchloric acid is not an oxidizing agent and behaves like dilute sulfuric acid.

Constant-boiling hydriodic acid of sp. gr. 1.70 is an effective reagent for certain "insolubles." The acid dissolves mercuric sulfide with evolution of hydrogen sulfide; ignited stannic oxide to form stannic iodide, which may be volatilized; the acid transposes the silver halides and forms soluble products with certain insoluble sulfates by reducing the sulfate radical.[1]

Dilute nitric and hydrofluoric acids (5 ml. of each concentrated acid per 30 ml.) dissolves many of the difficultly soluble compounds and alloys of tin, antimony, tungsten, or molybdenum; the action is rapid at about 80° C; a platinum vessel is used.

Fusions. Many substances are effectively decomposed only by fusion with an anhydrous mixture of either acidic or basic nature. One part of the finely ground refractory substance is intimately mixed with 8 or more parts by weight of the flux and fused in an appropriate crucible as indicated.

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[1] Caley, J. Am. Chem. Soc. **54**, 3240, 4112 (1932); **55**, 3947 (1933); Caley and Burford, Ind. Eng. Chem. Anal. Ed. **8**, 63 (1936).

(1) Sodium carbonate; or sodium and potassium carbonates in equal proportions. This flux decomposes most silicates, and it transposes the silver halides and the insoluble sulfates. A nickel crucible is used with salts of reducible metals and a platinum crucible in other cases.

(2) Sodium carbonate plus a small amount of an oxidizing agent, e.g., potassium nitrate, attacks sulfide ores and other substances (see Chapter XVI, p. 363 ff.). A nickel crucible is used.

(3) Sodium Peroxide. Sulfides and many refractory ores, notably those of chromium and tin are decomposed by this reagent; also certain alloys high in chromium and silicon. A nickel crucible previously lined with fused sodium carbonate is used.

(4) Sulfur and sodium carbonate in equal parts,—Rose's fusion mixture. It is used for the transformation of substances into sulfides and sulfosalts, and hence for the separation of Sn, Sb or As from mixtures containing compounds of Cu, Pb, etc. The fusion is made in a porcelain crucible, which is slightly attacked.

(5) Sodium or potassium hydroxide in molten condition attacks certain refractory ores, notably those of Sb, Cr or Sn. An iron or nickel crucible is used.

(6) Calcium carbonate (8 or more parts); ammonium chloride (1-1.5 parts). Used for the decomposition of silicates and the extraction of the alkalies. A platinum or nickel crucible of long tapered form is used.

(7) Potassium pyrosulfate or bisulfate. This is an acid flux which readily dissolves many ignited basic oxides, e.g., ferric oxide and alumina. It attacks ores of Al, Sb, etc.; also ferroalloys high in Mo, W or Cr. The fusions may be made in porcelain or platinum crucibles, preferably in the former.

After the fusion and cooling, the fused mass is extracted with water, or with dilute acid or alkali, according to the nature of the process. Whenever feasible the cooled melt is removed from the crucible as completely as possible before being treated with solvents.

In any process of such nature that violent action results, as for example action of acid upon a metal or a carbonate; action of reagents to liberate heat or to form gases, the vessel containing the weighed sample must be covered with a watch glass and the reagent added cautiously, little by little through the lip of the vessel.

8. **Preliminary Treatment.** This is so specialized and varies so much with the type of determination that the description is given under the various types of procedures.

9. **Precipitation** is discussed in detail in Chapter IX on Volumetric Precipitation Methods, and in the Chapters on the Theory of Precipitation, XV, and the practice, XVI. Titration is discussed in Chapter VI on The General Principles of Volumetric Analysis.

10. **Filtration and Washing.** Since these operations are required in certain preparative and volumetric processes as well as in gravimetric analyses, they will be discussed here.

Use of Filter Paper. A paper of special grade, previously extracted with hydrofluoric and hydrochloric acids to remove non-volatile matter is used. Such paper is removable by burning, after drying and separation from most of a reducible precipitate, or without previous drying and separation if the precipitate is not reducible. In gravimetric work a correction may be applied for the ash of such paper which commonly runs between 0.1 and 0.3 mg. for an 11 cm. paper. The value given by the manufacturer can be checked by selecting three to five typical sheets, i.e., sampling the pack, washing, drying, burning the papers in a weighed crucible and weighing the total ash; the total divided by the number of papers gives the average ash. Papers of various pore space or fineness and hardness may be obtained.

Filter pulp if added to a solution often greatly aids the filtration. The pulp is prepared by shaking with water a portion of a tablet prepared for this purpose, and the amount used in a single filtration leaves no weighable ash. Pulp may be prepared from a quantitative paper if the tablets are not available. The use of pulp largely avoids the necessity for several grades of paper, at least as far as introductory determinations are concerned.

The funnel and the receiving vessel must be perfectly clean, and for filtration by gravity the funnel should have a rather long stem (15-20 cm.). *The paper should be fitted to the funnel so perfectly that the stem of the latter remains filled with liquid throughout the filtration.* A funnel of the proper angle of 60°

is necessary. If a small corner is torn from the outside fold of the filter paper as shown in Fig. 6, it will fit the funnel more satisfactorily. A suitable assembly is indicated in Fig. 7. The top of the paper should be about 1 cm. below the rim of a large funnel, or proportionately adapted to other funnels. The liquid is poured down a glass rod, properly rounded at the ends, until the funnel is about three fourths full, never full to the top. The rim of clean paper about 0.5-1 cm. wide is essential in preventing loss of precipitate behind the paper, and also in the subsequent handling of the paper itself. The tip of the funnel touches the inside of the receiving vessel about 2 cm. below the rim. Filtrations that are made to remove insoluble matter must obviously be made as carefully as those in which a precipitate is to be recovered quantitatively and weighed. Material recovered by filtration should not be discarded, nor should a weighed precipitate until one is sure that no further tests need to be made upon it. A safe rule is not to discard such material

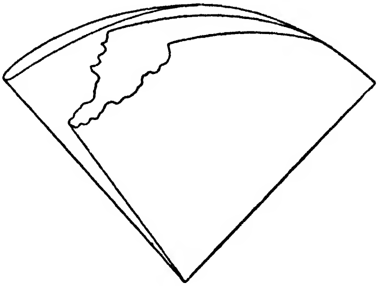

Fig. 6. Folded Filter Paper. The corner is torn off to make better contact with the funnel, behind the complete cone of the untorn portion.

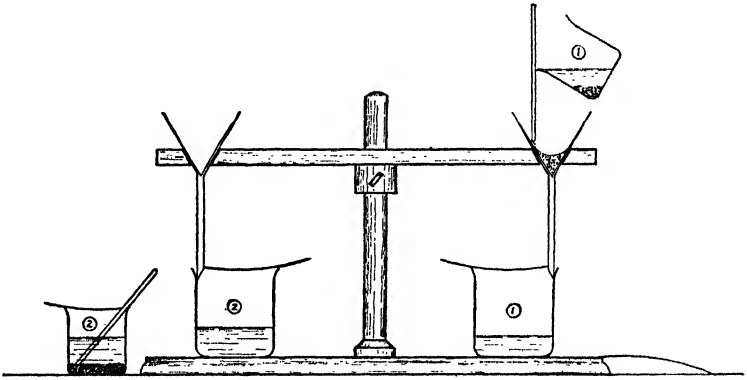

Fig. 7. Filtration Assembly. Filtration on paper, showing the use of stirring rod and the protection of the filtrate.

until the analysis has been reported and the report considered. For example, ferric oxide frequently carries silica derived from the ammonium hydroxide bottle. The precipitate should be dissolved in hydrochloric acid and the silica if present may be recovered, and weighed.

The method of transferring the last traces of the precipitate to the filter is indicated in Fig. 8. If this method fails a policeman or a properly trimmed feather is used. If paper is being used, the particles that adhere to the rod and beaker may be wiped off with successive small portions of a quantitative paper moistened with distilled water. If necessary a correction may be applied for the ash thus introduced. Finally, any of the precipitate that has not been transferred by any of the foregoing methods may in some cases be dissolved in a few drops of an appropriate solvent and reprecipitated; this method is preferably avoided because it prolongs the washing process.

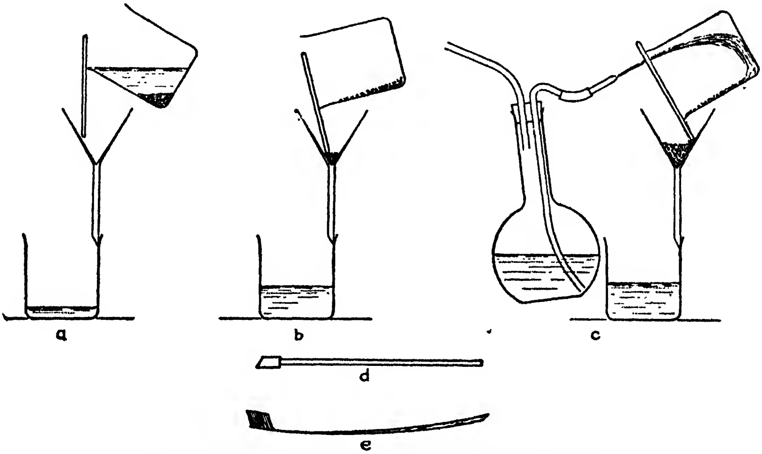

FIG. 8. Transfer of Precipitate to Filter Paper.

a. Decantation of the liquid.
b. Removal of the major part of the precipitate.
c. Washing out the remainder of the precipitate.
d. A rod tipped with rubber; used as a "policeman" to loosen particles of precipitate.
e. A feather trimmed for use as a "policeman."

Filtration by Suction. Common devices for this purpose are indicated in Figs. 9 and 10. The use of a safety bottle as indicated in Fig. 9 is to be recommended in all filtrations when suction is applied by a water pump. The paper must be sup-

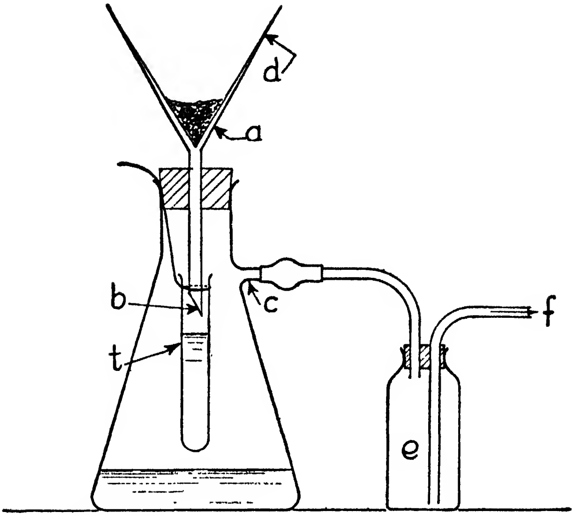

Fig. 9. Filtration by Suction.

a. Supporting cone. *b.* Funnel tip, which extends below *c*, the side arm of the receiver. *d.* Upper edge of filter paper. *e.* Safety bottle. *f.* Connection to the suction line. *t.* Test tube, held in place by a wire or a string; used to collect small portions of the washings for testing purposes.

ported by a cone of hardened paper, perforated platinum foil or other suitable material. The use of a bell-jar has the advantage that the filtrate may be received directly in the vessel in which the next process is to be carried out. This method of filtration is of especial value in electrolytic work where the receiver usually ranges from 150-250 ml. (see Chapter XX). Materials other than glass may be used for funnel and receiver, as for example hard rubber for the filtration of solutions containing fluoride.

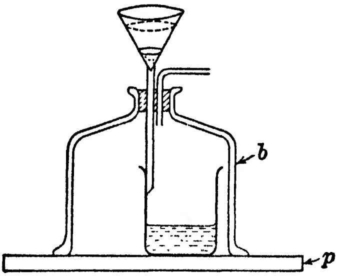

Fig. 10. Suction Filter.

The plate; *p*, has a ground-glass surface, against which the ground rim of the bell-jar, *b*, makes an air-tight seal, with the aid of vaseline or stopcock grease.

The Use of Filtering Crucibles. Crucibles with porous filtering beds of various materials are useful in preparative work for filtration of solutions which attack paper, as for example a solution of potassium permanganate. They are important devices for the collection of precipitates which are to be weighed or dissolved and the solutions titrated.

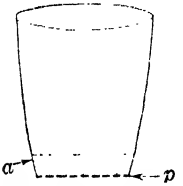

FIG. 11. A Gooch Crucible.

The perforated bottom, *p*, is covered with an asbestos filter mat as described on p. 30.

Gooch[1] proposed the use of a platinum crucible having a number of fine perforations in the bottom, Fig. 11, which is covered with especially treated asbestos. This idea represents an important advance in technique because the precipitate is collected in the previously weighed filtering crucible and washed, dried and weighed therein. The earlier practice of drying and weighing a filter paper had obvious limitations because many precipitates can not be brought into a reproducible state at the low temperature which paper will withstand; also the paper itself is apt to change in weight during the washing and drying operations.

Munroe and later Neubauer[2] proposed the use of a permanent layer of spongy platinum instead of the asbestos, which must be replaced after one or at most a few determinations. Porcelain crucibles of the Gooch type have long been useful and popular. Brunck[3] devised porcelain filtering crucibles with a filtering layer of spongy platinum. In all cases the spongy platinum is deposited, repaired or replenished by heating ammonium chloroplatinate moistened with alcohol; upon gradual and then strong heating the platinum is left in a porous coherent mass.

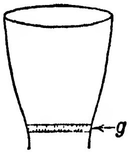

FIG. 12. Glass Filtering Crucible.

g is a layer of glass particles sintered together to give a filtering medium of any desired porosity.

Glass filtering crucibles have been developed by the Jena glassworks in Germany, Fig. 12. The filtering medium is of sintered glass.[4] This type is very useful for certain purposes but may not be heated above 500-600° C., and can only be heated to that range by gradual application of heat and gradual cooling.

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[1] F. A. Gooch, Proc. Am. Acad. Sci. **13**, 342 (1878).

[2] Munroe, J. Anal. Appl. Chem. **2**, 241 (1888); Neubauer, Z. anal. Chem. **39**, 501 (1900).

[3] Brunck, Chem. Ztg. **33**, 649 (1909).

[4] Similar crucibles are made by the Corning Glass Co., Corning, N. Y.

The crucibles are available in several sizes and porosities. Those of designation mark ending G3 have an average porosity of 20-30 microns[1] and those ending in G4 of 5-10 microns. These are suitable for ordinary and rather fine analytical precipitates.

Royal Berlin Porcelain crucibles with porcelain filter bed sintered into the bottom are available. If not subjected to too sudden thermal or mechanical shock these crucibles may be heated to bright redness, preferably by means of an electric furnace that can be heated and cooled gradually. When heated by a gas flame any type of filter crucible has to be protected at the bottom by an ordinary porcelain crucible or other adequate device.

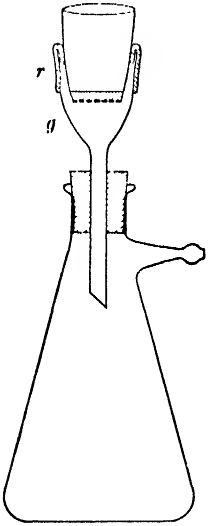

Fig. 13. Filtering Assembly.

g. Glass holder.
r. Rubber tube so adjusted that the liquid passing through the crucible does not come into contact with the rubber.

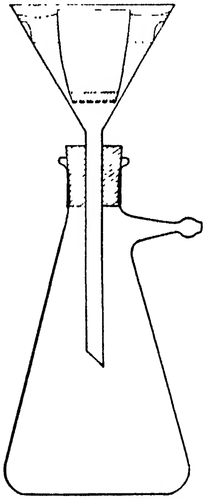

Fig. 14. Filtering Assembly with Rubber Ring to Hold Filtering Crucible.

Both glass and porcelain crucibles are slowly but seriously attacked by sodium hydroxide solutions from 0.125 N up in 2 hours at boiling temperature.

With any type of filter crucible a special holder is necessary, as shown in Figs. 13 and 14. All filter crucibles are dried at the

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[1] A micron is 0.001 mm.

same temperature that will be used later in drying the precipitate. The filtering media retain different amounts of superficially bound water at various temperatures. For example, a difference of 1 mg. may be found if a crucible dried to apparent constant weight at 100-105° C. is heated to redness, cooled and weighed. The transfer of precipitates to filtering crucibles follows the same principles that have been described for filtrations through paper, p. 25 and Fig. 8, p. 26.

The Preparation of a Gooch Crucible. A special grade of rather long-fibered asbestos is commercially available; it has been treated with hydrochloric acid and will serve for most purposes.[1] Make a suspension of asbestos in distilled water by putting enough of the dry material into a bottle to fill it about one fourth full and then adding water nearly to the top. Shake or stir the mixture vigorously. Clean the Gooch crucibles and mark them for identification, as described on p. 12. The holes should not be too large, otherwise a loss of asbestos will occur; a diameter of 0.5 mm. is very satisfactory. Place the crucible in a suitable suction filter apparatus, and without applying suction pour in an amount of the well-shaken asbestos suspension which will eventually form a mat 0.5 to 2 mm. in thickness. The proper amount of the asbestos to use must be found by experiment. A thin mat will filter better than a thick one and is to be preferred unless the precipitate is unusually fine-grained. Allow the suspension to settle two or three minutes so that the larger particles will settle to the bottom. In order that this may take place the suspension should not be too thick, the liquid filling the crucible two-thirds full. Apply suction gently to form an even layer of asbestos on the bottom of the crucible. When the perforated end of the crucible containing the wet mat is held toward a strong light the thickness of the mat should be

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[1] If further purification is desired, the following method is recommended: Allow the asbestos to digest with 1 : 1 hydrochloric acid for several hours at 80–90° C., and then wash with water until the acid reaction is faint. Allow the asbestos to digest with 20 per cent sodium hydroxide under the same conditions as during the acid treatment; wash until the alkalinity is faint. Repeat the treatment with acid and wash thoroughly with water. Washing by decantation may be made semi-automatic in a large bottle or cylinder when large quantities of asbestos are treated. It is more efficient for an assistant to prepare a large quantity of the asbestos than for individual students to prepare small lots.

just sufficient to make the holes invisible. Use about 100 ml. of water in small portions to wash out the fine particles and soluble matter. Never pour any liquid into the crucible unless suction is being applied or the mat will be torn and run through; the liquid is, of course, poured down a rod and allowed to fall gently in the center of the crucible. Remove the crucible without turning off the suction pump; this may be done by disconnecting the side tube from the filter flask. Wipe the outside of the crucible and dry it at the temperature that will be used subsequently in drying the precipitate. If a high temperature is to be used, most of the water is removed by careful drying at a lower temperature before the maximum temperature is applied.

If it is difficult to prepare a rapid filtering mat, a small amount of glass wool or glass cloth if applied before the asbestos is put in will speed up the filtrations. This device and the tamping down of the asbestos with a flattened rod were recommended in some of the early descriptions of the method. They should be unnecessary if the pores of the crucible are of proper diameter. The use of silica cotton and glass cotton has been recommended for Gooch filters instead of asbestos.[1]

Washing. This topic is further discussed in Chapter XV, p. 301. In brief, water is used whenever its use is permissible, and near the boiling temperature if the nature and solubility of the precipitate will permit. Very frequently it is necessary to use a special wash fluid either to make the precipitate less soluble or to prevent it from going back into colloidal suspension. The wash liquid is used in small portions, each of which is allowed to run through before the next is applied. A qualitative test for some ion is made to check the completeness of the washing. If the filtrate is to be discarded any convenient test may be applied. If the filtrate is to be used further, the qualitative test must be one which will not add undesired substances. Experience has shown that after 6 to 8 washings made in the correct fashion the amount of material that is lost in the next few drops of the wash liquid that are collected and used for a test is of little consequence. Tests that make possible the recovery of the material may be devised.

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[1] W. W. Russell and J. H. A. Harley, Jr., Ind. Eng. Chem. Anal. Ed. **11, 168** (1939).

11. **The Heating of Crucibles.** The final handling of precipitates in gravimetric analysis is further considered in Chapter XV, p. 304. In general the crucible or other vessel that is to be used in the final weighing is heated initially at the same temperature and in the same manner that will be used later. As has been explained, filter crucibles other than platinum weigh roughly 1 mg. less if brought to constant weight by heating at 700-800° C. than if brought to apparently constant weight at 100-105° C. During the marking of crucibles or their heating in a flame they should always be supported on a triangle so that the crucible is in contact with clay, silica, nichrome or platinum; a wire gauze should never be used instead of the triangle. A ringstand which is adjustable is more suitable than a tripod. The ring, triangle and crucible are so placed that with the flame that is used the

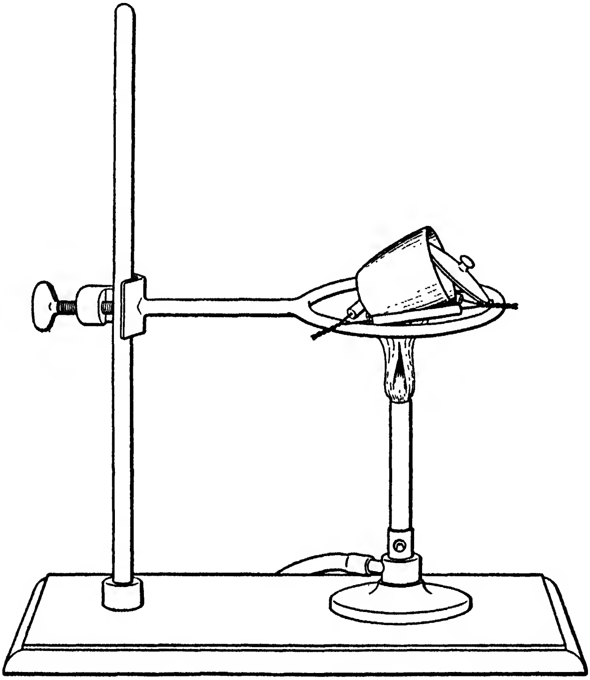


Fig. 15. Special Position of Crucible and Lid. This position is used after the major portion of the filter paper has been slowly carbonized with the crucible in the upright position with the lid almost covering it. The slanting position is also useful during the burning in of identifying marks.

bottom of the crucible is in contact with a blue oxidizing flame. If a burner chimney is provided its use is advantageous. The use of a yellow flame, or the placing of the bottom of the crucible in the cone of unburned gas should be avoided; the deposit of soot which would form is only slowly burned in the oxidizing flame. After the crucible has been heated long enough to remove moisture and to burn off the carbonaceous matter from the ink or other sources, it is allowed to cool until the red glow has vanished, and then immediately placed in a hole in the desiccator plate. Contact of the hot crucible or its lid with the desk top, a wire gauze or asbestos board will often leave stains that are difficult to clean. A special position of a crucible and its lid is indicated in Fig. 15; with the crucible slanted in this fashion the lid deflects a mild stream of air over the contents, thus maintaining the oxidizing conditions that are important in removing the last bits of carbonized paper, reoxidizing partially reduced material, etc.

If a blast lamp is to be used, a well-regulated oxidizing flame is applied after a preliminary warming of the crucible. The blast flame is directed up at an angle of about 50° to the desk top to strike only the bottom of the crucible which is slanted up and out at approximately a right angle to the line of the flame, so that the top and lid are protected from any direct draft which might cause mechanical loss of the precipitate. The use of a burner of the Meker type gives a high temperature without danger of mechanical loss and without attention, whereas the blast flame often varies due to pressure changes in the air line. Properly designed electric muffles and furnaces, if available, are clean and effective for igniting precipitates and are especially effective because they maintain an oxidizing atmosphere and because their temperature can be controlled and measured. As has been stated, a filtering crucible is always heated within another vessel as indicated in Fig. 16. If a flame were allowed to play directly upon the bottom of the

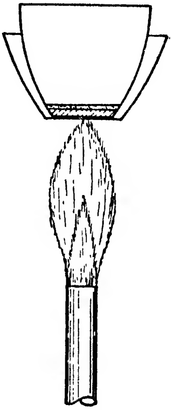


FIG. 16. Heating a Porcelain Filter Crucible. The asbestos layer and the precipitate are protected from the direct action of burner gases by the outer crucible.

crucible it might cause undesirable chemical changes due to reduction, for example, and would probably injure the filtering medium.

12. **Calculations.** The methods of calculation that are used in Volumetric Analysis are explained in Chaps. VII, VIII, IX, X, and XI and those of Gravimetric Analysis on pp. 306-314. Under the heading "Calculations" in the Index will be found a complete list of the individual kinds of calculations.

CHAPTER III

THE BALANCE. WEIGHING. CALIBRATION OF WEIGHTS A SIMPLE QUANTITATIVE EXPERIMENT

THE BALANCE

The Analytical Balance. The essential parts of an analytical balance are indicated in Fig. 17. The beam, A, is a lever of the first class with fulcrum as nearly as possible equidistant between the terminal knife edges. When in motion the beam, pans, weights and object move according to the manner of a compound pendulum,—that is, with harmonic damped oscillation. The beam is supported when the balance is not in use and when weights and objects are placed upon or removed from the pans, in order to prevent damage to the knife edges and planes against which they bear; both edges and planes are of agate in the more sensitive balances. The beam support, S, is generally operated by a control milled head, B, at the front of the floor of the balance. Pan supports, covered with felt or other suitable material, engage the bottoms of the pans. The supports are sometimes operated in unison with the beam support and sometimes by a separate lever system terminating in a button, P, at the left of the central milled head. Supports of the latter type are often designed to yield when the load on one pan is a gram or more heavier than that on the other.

The distance from the fulcrum to a terminal knife edge is the power arm of the lever. It is most frequently divided into either 5 or 10 equal divisions; some balances have 6 or 12 equal divisions. If f_1 and f_2 are the forces applied at the outer knife edges and if d_1 and d_2 are the respective distances, then at equilibrium $f_1 \times d_1 = f_2 \times d_2$. If a balance has, for example, six divisions out to the terminal knife edge, and it is desired to have the rider, *r*, Fig. 17, indicate 1 milligram when placed at 1, two at division 2, etc., then we see that a 5 milligram weight if placed on the left pan will exert a moment of 5 × 6, and this is to be balanced by the rider at division 5, or $5 \times 6 = r \times 5$, whence $r = 6$, that is, a 6 milligram rider would be used with this balance.

It will be observed that the process of weighing in quantitative analysis is really one of comparing masses and not one of determining the attraction of gravity upon these masses. The masses that are used are commonly called weights and the process of determining the unknown masses is called weighing. Although the pull of gravity varies with the latitude, analysts working upon the same material at widely different latitudes and altitudes will in general not disagree by as much as 0.01 per cent due to neglect of this factor.

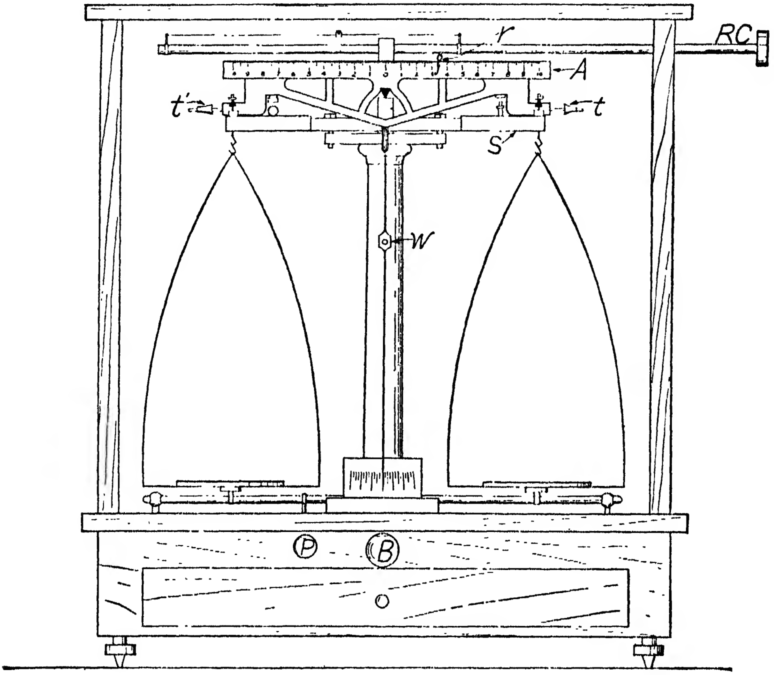


FIG. 17. Analytical Balance.

A.	Beam.
B.	Head of beam release.
S.	Supporting lever for beam and stirrups; operated by B.
P.	Pan release.
r.	Rider shown on right at 3.4 milligrams, i.e. 0.0034 gram.
t, t'.	Adjustment screws to bring pointer to the middle of the scale.
W.	Weight on pointer provided for adjustment of sensibility by changing the center of gravity of the beam system.

With an equal-arm balance of the type that is commonly used the observations finally consist in noting turning points or inflections of the pointer, attached to the beam, against a white scale at the base of the beam post, and interpreting the data in terms of a previously determined sensibility table, p. 46. The following types of balances are designed for greater speed, convenience or accuracy. Although it is not ordinarily possible to supply these instruments for course instruction their use should be considered whenever circumstances permit or justify it.

The Balance with Magnetic Damping. The necessity of reading a number of pointer inflections is eliminated by damping devices which cause the pointer to move slowly to its equilibrium position and stop. Ten to fifteen seconds is usually required. Damping causes no decrease in sensitivity because this force decreases as the pointer comes to rest. The damping effect of currents induced in a metal plate moving freely between the poles of a powerful permanent magnet is an excellent time-saving device. The balance may be of conventional type, with detachable damping devices consisting of an aluminum plate and supports attachable to one stirrup, and a counterpoise attachable to the opposite one. The magnet is mounted either upon the central post of the balance or upon a special support

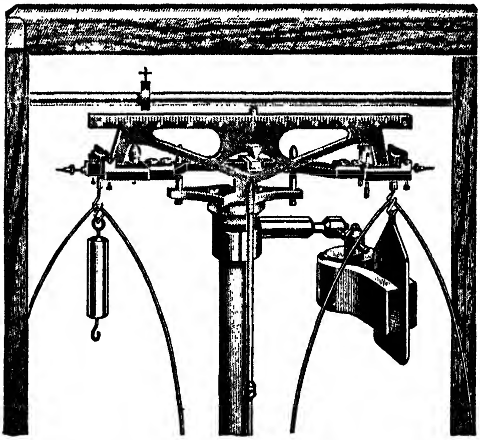


FIG. 18. Magnetic Damper. Illustrating a detachable plate and counterpoise.

(Courtesy of Seederer-Kohlbusch, Inc.)

readily removable from the balance case. Other balances are built especially for this application and have other time-saving devices built in during their construction. They have provision for weighing easily either with or without the damping action. Fig. 18.

The Air Damped Balance. In this type of balance the damping effect is produced by large light pistons attached to pan or beam and moving loosely in cylinders, or by vanes moving in cylinders. The general damping characteristics are the same as with the magnetic device.

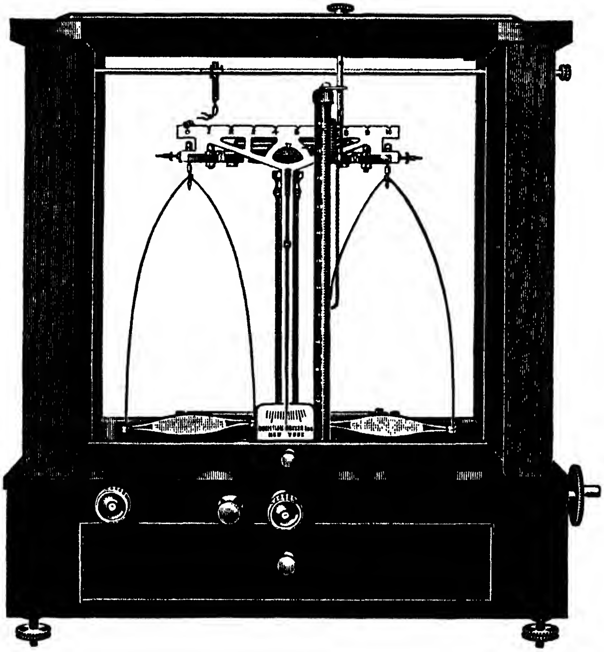
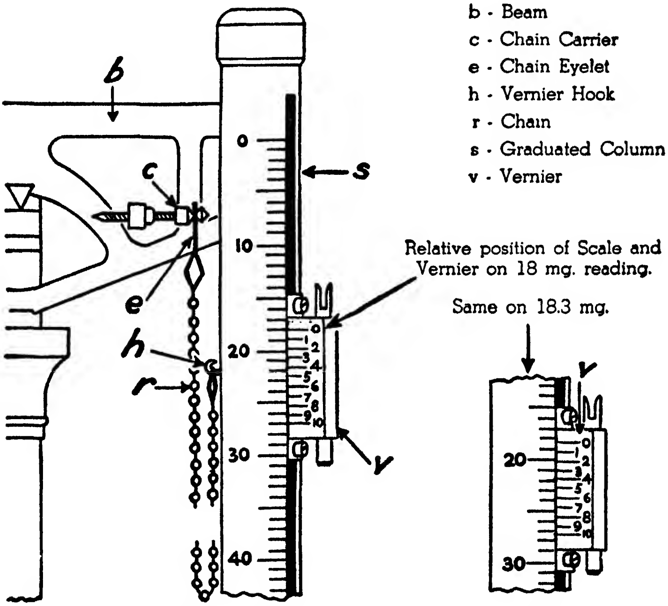


Fig. 19. A Chainomatic Balance.

The use of balances with damping devices can be recommended very highly. Other devices which save time in weighing usually avoid the shifting of weights manually, as in the following two designs.

The Chainomatic Balance. This type has a suitable metal chain one end of which is attached to the beam of the balance and the other to a movable vernier that may be moved vertically along a calibrated post in the balance case, thus adding or removing weight. The device is operated by a control outside of the case. The general features are indicated in Fig. 19. In one modification of the balance the weights are placed on the right pan to the nearest tenth of a gram below the weight of the object. The last three places (hundredths, thousandths, ten thousandths of a gram) are found with the aid of the chain and the vernier. In other chainomatic balances less handling of small weights is necessary.

View of Portion of Balance showing Graduated Column and Vernier and Method of Attachment of Chain.



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

Same on 18.3 mg.

Fig. 19(a). Graduated Column and Vernier. (Courtesy of Christian Becker, Inc.)

Multiple Rider Balances. In Fig. 20 is shown a balance in which the various weights, some of them constructed in the form of riders, are put in place or removed by individual levers. The advantages of this rather expensive type of construction are the speed of operation, the precision with which the weights may be placed in the same positions, and the saving of wear on the weights.

Microbalances. Balances of special construction, Fig. 21, have been used in the development of microanalytical methods. It is possible to use standard balances of proper sensibility in this field of work; slightly larger samples are used than with the special balances.[1]

Accuracy of the Balance. The following conditions are necessary for the accurate and dependable performance of a balance:

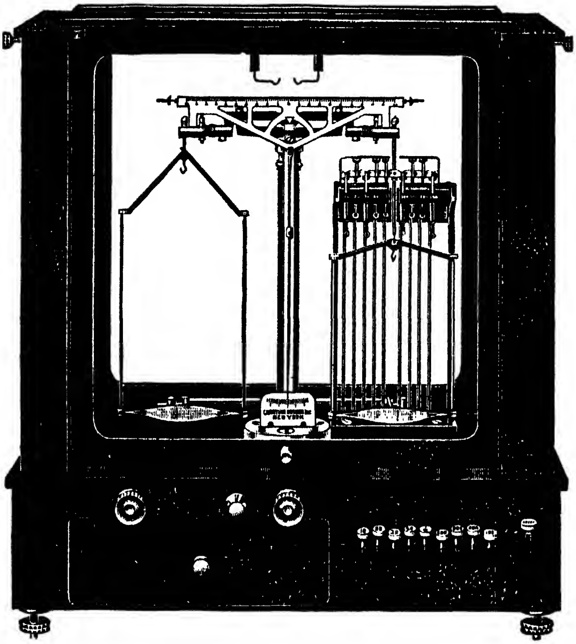


FIG. 20. Keyboard Rider Balance.
(Courtesy of Christian Becker, Inc.)

1. The knife edges must be parallel and in the same plane. If the knife edges of the pan supports are above the fulcrum it is possible to bring the beam system into non-oscillating equilibrium with sufficient loading.

2. The beam must be sufficiently rigid to carry the maximum load for which it is designed without appreciable bending. This condition is of course involved in the necessity that the knife edges remain in a plane.

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[1] J. B. Niederl, V. Niederl, R. H. Nagel and A. A. Benedetti-Pichler, Ind. Eng. Chem. Anal. Ed. **11**, 412 (1939).

3. The point of support or central knife edge of the beam must lie above the center of gravity of the beam system. If it were at the center of gravity non-oscillating or neutral equilibrium would result; if it were below, the beam would be top-heavy, and would not oscillate. Analytical balances are so carefully constructed that a slight movement of the movable weight, *w*, Fig. 17, along the pointer is sufficient to cause an appreciable vertical shift in the center of gravity of the beam system. This weight is adjusted properly in advance and left untouched during many months of work of a given nature.

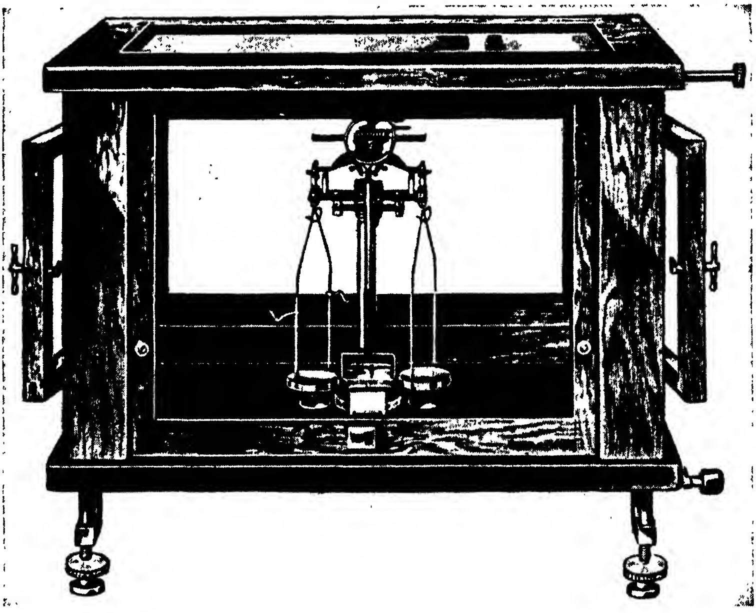

Fig. 21. A Microbalance.

Sensibility of the Balance. Sensibility is defined in terms of displacement of the pointer, attached to the beam, per unit of weight, usually a milligram, added to one pan. It is frequently expressed in weight indicated by a displacement of one division on the scale at the base of the beam. The factors of balance construction which affect the sensibility are:

1. *Friction,* which must be at a minimum. Agate knife edges and planes are used to eliminate friction. A glass case prevents external air currents from affecting the motion of the system. Without such protection irregular frictional effects are produced. Hence in the final readings of pointer inflections or turning points the case is always kept closed.

2. *Length of the beam* as a whole and hence of the arms of the lever. Other things being equal, the longer the power arm the greater the displacement per milligram, i.e., the sensibility. A long beam leads to a long period of oscillation; there must therefore be a compromise among desirable factors in order to have desirable operating characteristics.

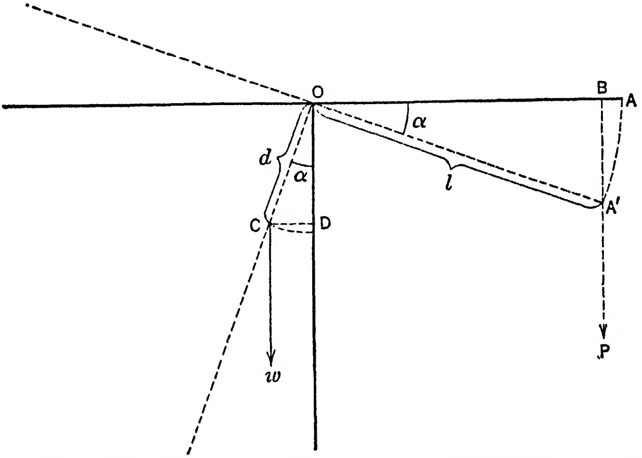

FIG. 22. Diagram Showing Effect of Constructional Factors on the Sensibility of a Balance.

3. *The weight of the beam* should be small. The lighter the beam the less is the restoring moment operating against a given excess of weight on one pan. This condition places a limit upon the length of a beam of any given material.

4. *The distance between the center of gravity of the beam and the center of support* of the beam should be small. The smaller this distance the lower the restoring moment and the more sensitive the balance.

The length of the pointer and the construction of its tip and the scale against which displacements are read are factors which affect the ease of determining sensibility and weight. An inexpensive lens mounted on metal or weighted wood or cork is of assistance in reading turning points.

The relations (2–4) may be understood more fully by a study of Fig. 22. The opposing forces which tend to cause the beam system to oscillate when set in motion are the small excess weight, P, acting on one pan and the weight, w, of the beam regarded as if acting downward at a point which is slightly displaced from a vertical line through the central knife edge or fulcrum, O. If the point of rest with the excess load, P, on the right corresponds to an angular displacement, α, of the pointer, the two equal and opposed moments at this point are represented by $w \times CD = P \times OB$. The angles AOA' and COD are equal and are equal to α; hence $\frac{OB}{l} = \cos \alpha$, or $OB = l \cos \alpha$, l being the length of the power arm of the balance. And $\frac{CD}{d} = \sin \alpha$, or $CD = d \sin \alpha$, d being the distance from the central knife edge to the center of gravity of the beam. Then $w \times d \sin \alpha = Pl \cos \alpha$, or $\frac{\sin \alpha}{\cos \alpha} = \tan \alpha = \frac{P\,l}{w\,d}$. For small angles α and $\tan \alpha$ are proportional and hence the angular displacement for a given value of P is greater the longer l, the smaller d and the smaller is w. One milligram is the value generally selected for P.

The following rules should be observed in the use of the balance-room and balances:

1. Students assigned to a balance are responsible for the neatness of that balance and its immediate surroundings.

2. The balance case is left closed when the balance is not in use in order to protect it from dust and fumes.

3. Neither weights nor other objects shall be placed upon or removed from the balance pans unless the beam and pans have been supported by the support mechanisms.

4. Hot objects, moist objects and liquids must never be allowed to come into contact with pans or weights. Crucibles should be inspected for absence of soot from a smoky flame before being placed in desiccators.

5. The object that is weighed must be at the temperature of the balance. Porcelain crucibles require at least 30 minutes in a desiccator to cool from 700°–1000° C. to room temperature.

6. The beam support and the pan supports must be raised and lowered gently to avoid damage to the agate knife edges.

7. The balance door must be closed while the final adjustment of the rider is being made and while the swings are being observed. The rider should be lifted up on the rider carrier when the weighing is finished or placed at the center of the beam.

8. The weights must never be touched with the fingers. The ivory-tipped forceps must be used for handling the weights *and for no other purpose.*

9. The door of the balance room should be kept closed as much of the time as possible to exclude dust, fumes and drafts.

10. An instructor in the course should be notified if a balance is in need of adjustment.

Resting-Point and Deflection. Most methods of weighing involve the determination of either the initial *resting-point* or the *deflection* of the pointer with no load on the pans and with the rider lifted from the beam. By *resting-point,* often called zero point, is meant the position at which the pointer would come to rest. With a balance damped magnetically or by pistons (see pp. 37-38) this point is determined directly; when the beam and pans are released the pointer tip comes to rest in a few seconds and the position is noted, e.g., +0.4 or −0.7 etc. Without damping the time required would be very long and the value found probably erroneous due to irregular frictional effects. Therefore the resting-point is calculated from a few successive readings of the turning points of the pointer, omitting the first two swings after releasing the beam. An *odd* number of turning points is read to give a whole number of complete swings of the balance. The left-hand readings are read relative to the center of the pointer scale, and averaged and likewise the right-hand ones. The resting-point is taken as the mid-point between the two average values. Example:

	Left readings (−)		Right readings
	−3.9		4.5
	−3.6		4.2
	−3.3	Sum	8.7
Sum	−10.8	½ Sum	4.4 av. (rounded)
⅓ Sum	−3.6 av.		

$$\text{Resting-point} = \frac{-3.6 + 4.4}{2} = 0.4$$

The left-hand readings are arbitrarily called negative ones.

Deflection. The observations are taken exactly as for the resting-point, and the left-hand and right-hand averages are obtained. The deflection is the algebraic sum of these two averages. In the illustration just given the deflection is $-3.6 + 4.4 = 0.8$ "The deflection may be defined as the other point of inflection" (turning point) "of an ideal swing having zero for one point of inflection."[1] The deflection is always twice as far from the central scale division as the resting-point. The use of deflections rather than resting-points is universal in microchemical work and it has been adopted here as a method that will cover all types of weighing in which turning points are read with an undamped balance.

Testing the Rider. Sets of weights are often equipped with spare riders that may not be proper for the balance that is in use. Whenever a rider is used for the first time it should be tested. Having obtained the deflection, as in the preceding paragraph, place the rider on the division near the right end of the beam marked 10 (or 5 on short-arm balances). Place a 10 mg. weight on the left pan (or a 5 mg. one if the division is marked 5). Upon releasing the beam and determining the deflection by the method of reading five turning points, averaging, etc. the value that is found should be within a few tenths of a division of that found for the empty balance. If there is a serious discrepancy the defective rider is to be replaced.

Determination of the Sensibility of the Balance.[2] The sensibility may be defined as change in deflection per milligram of mass. It varies with the loads in the pans, and hence it is customary to find it for several loads. The procedure is to determine the deflection at the load in question; immediately thereafter the deflection is redetermined after placing the rider at division one, or after moving it one major beam division if it is already in use. One milligram is thus added to one of the pans.

The sensibility should be determined at loads of 0, 10, 20 and 30 g. in each pan, and if circumstances permit also at loads

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[1] A. A. Benedetti-Pichler, Ind. Eng. Chem. Anal. Ed. **11**, 226 (1939).

[2] If a damped balance is used the change in resting-point that is caused by the addition of 1 milligram is found for the various loads. Since the change in resting-point is half as great as the change in deflection, the weight per division will be twice that which would be found by the deflection method.

of 40 and 50 g. A table may be constructed and placed in a convenient place in the notebook, as follows:

Load on each pan, grams.	*Change in Deflection per milligram*	*Weight in gram per 1 division deflection of pointer (rounded)*
0	6.0	0.00017
10	5.6	0.00018
20	5.4	0.00018
30	5.0	0.00020
40	4.4	0.00023
50	4.0	0.00025

For macro-scale weighings an average value of 0.00018 g. might be used for this balance for all loads from 0–30 g. It should be pointed out that the use of the resting-point displacement method instead of deflection would give figures divided by two in the central column of the preceding table, e.g., 3.0, 2.8, etc., and the sensitivity data in the third column would then be 0.00034, 0.00036, etc.

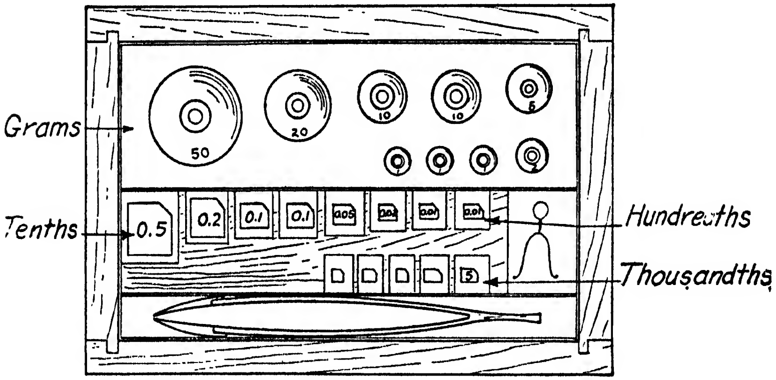

FIG. 23. A Set of Analytical Weights. Sets may be obtained in which no two pieces are alike, as for example with gram weights: 1, 2, 3, 5, 10, 20, 30 and 50.

The Weights; Weighing. A typical assortment of weights is indicated in Fig. 23. The pieces from 1 g. up are usually of brass thinly lacquered to prevent corrosion. The fractions run from 0.5 g. down to 0.01 g. if the beam has ten or more divisions on one arm, and down to 0.005 g. if a balance with a 5 division arm is used. The fractions may be of platinum or tantalum, or more commonly of aluminum for the smaller ones. The rider, frequently of aluminum, is used for adding the milligrams that are needed after the weight has been found to the nearest 0.01 g. The last place (ten thousandths of a gram) is, in general, determined from the deflection and the predetermined sensibility table.

Weighing. The object to be weighed is placed on the left pan and the weights on the right. The weights are put on systematically, first a weight estimated to be heavier than the object, e.g., 20 g. If this is too heavy, 15 g. is tried and so forth. The weights are always kept in the same position in the weight box. In some sets of weights there are no duplicates. If there are two weights of the same denomination, the same one of these is always used when only one weight of this denomination is required. Distinguishing marks such as stars or asterisks are usually put on the two ten g. weights, etc., by the manufacturers. The weights are handled only with the forceps provided; the forceps are never used for any purpose except to handle weights.

Weighing by Difference. It is helpful to know approximately the amount of material in a weighing bottle. The weights of the available bottles may be found rapidly in advance to the nearest 0.1 g. and noted in the notebook. When a sample of a dried powder is to be weighed, the stoppered weighing bottle is transferred from the desiccator, where it was placed after drying, to the left balance pan and weighed. The bottle is handled with a small piece of clean paper, cloth or chamois skin to avoid grease from the fingers. The stopper is loosened momentarily to be sure that the air within is at atmospheric pressure. The proper amount of the material is either allowed to fall into a clean beaker or other vessel or removed with a clean spatula and transferred to the vessel, using, if necessary, a clean camel's hair brush. The stopper is immediately replaced and the bottle reweighed, the weight being noted again. The difference in weights gives the weight of the sample. A third weighing after removal of a second sample gives the weight of the second sample, and so on. *Three samples* are generally carried through any analysis and the beginner is advised to use this number. A very simple practice determination like an experiment in quantitative drying may safely be attempted with two samples. It is very important that every particle removed from the bottle be transferred to the numbered beaker or other vessel that is to receive it. The transfer should be performed with the open end of the bottle held over the vessel.

It is not advisable to attempt to weigh out exactly 1 g. or definite fractions or multiples. If the directions call for 0.5 g. anything from 0.4 to 0.6 g. is intended and even larger variations are sometimes permissible. In volumetric standardizations the amount weighed should require from 35 to 50 ml. of the solution to be standardized. If samples used are too small the percentage error may be greater, and with too large a sample precipitates may be bulky and difficult to wash, or too many buret readings will be required in a volumetric determination.

The method of weighing by difference that has been described is used for all substances except metallic shavings, such as brass, bronze or steel, which need no drying and may be weighed directly on a watch glass, celluloid plate or metal scoop, placed directly on the pan of the balance. All fine powders, even if not hygroscopic by nature, will take up moisture when exposed to the air, and therefore should be weighed in a properly closed container. With hygroscopic substances this error would of course be larger. The directions that have been given apply to all unknowns and will not be repeated.

When the weight of an object has been found the weights on the pan are counted and checked against the empty positions in the weight box. All weights are recorded at once in ink in the proper place in the notebook and never on loose scraps of paper. The latter is a most pernicious habit which has been the cause of much loss of time and many errors.

The following are some sources of error in weighing, with brief indication of the methods of avoiding or compensating for them.

SOURCES OF ERROR

1. **Buoyant Effects Due to Various Causes.** (*a*) *Displacement effects.* Both object and weights are buoyed up by the air that they displace and hence to different degrees if their volumes are different. A calculated correction may be made for this effect when needed; see p. 54. This effect is properly taken into account in calibrating volumetric glassware, Chap. VI. In most analytical determinations it is a second order effect. With

large objects the effect is minimized by using a counterpoise as nearly as possible identical in size and content with the object, as in carbon dioxide determinations, Chap. XVIII. A counterpoise also helps to correct for changes in atmospheric humidity between weighings.

(*b*) *Temperature effects.* The object is always allowed to reach the temperature of the balance before it is weighed. If it were warmer a serious error would result due to convection currents, making the object appear lighter than it is; if colder, convection currents that would make it seem too heavy would be set up and moisture might condense upon it.

(*c*) *Closed vessels.* The air in a closed container such as a weighing bottle that has been stoppered while warm is at a pressure lower than atmospheric when cold if it is airtight. As a precaution the stoppers of such vessels are always opened momentarily before the bottle is weighed. Absorption vessels taken from a gas train may be filled with oxygen, nitrogen, hydrogen, etc. The gas may not be at atmospheric pressure. Before weighing, these vessels are either filled with dry air at atmospheric pressure, or with the same gas at the same temperature and pressure before and after the absorption process.

2. **Substances Taken up from the Atmosphere.** Moisture, carbon dioxide, dust and oxygen are the chief components of the atmosphere that may alter the weight of a substance while it is cooling or being weighed. Balances are placed in separate rooms, sometimes air-conditioned, or in special hoods in order to protect them from dust and fumes that are prevalent in large laboratories. Simple weighing bottles or more elaborate ones that may be evacuated or filled with inert gases are used to protect substances from atmospheric agents. The containing vessels, especially if large, may condense or adsorb a serious amount of moisture depending upon the relative humidity. The most effective means for compensating this effect in a simple way is to use a duplicate vessel as a counterpoise. It is important that the counterpoise be filled to the same extent and with material of the same specific gravity as the object.

3. **Electrification.** The wiping of glass containers with a dry cloth may leave the surface electrified with a charge that takes 10 to 15 minutes to become dissipated. The action of the charge upon the balance pan or the neighboring metal parts may

cause an error approaching 0.1 g. in magnitude if attempt is made to weigh it immediately after wiping it. In continuous work with very large glass objects it has been found that a little of a radioactive preparation if placed in the balance case will aid in the dissipation of the surface charges.

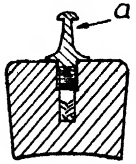

FIG. 24. An Analytical Weight. For adjustment, the head, *a*, is removable, 0.1 or 0.05 mg. pieces may be added to the cavity below it, or the bottom of the screw may be removed by filing.

4. **The Weights** may be in relative disagreement, or may be inaccurate. The remedy is calibration as described on pp. 55-60. If values on a true gram basis are needed a weight calibrated by the National Bureau of Standards against a known mass may be included in the calibration of the set. Weights may be adjusted to relative agreement with the aid of a set of equipment designed for that purpose. See Fig. 24.

5. **The balance arms may be unequal.** This is without effect upon quantitative analysis if the object is always placed upon the left pan. The inequality may be found experimentally as described under Arm Ratio, p. 54, or the Gauss Method, p. 53, or the Borda substitution method, p. 54 may be used when true rather than relative masses are of importance.

6. **Latitude and Altitude.** The distance from the center of the earth to the balance pan varies with the latitude and with the altitude above sea level. As has been stated, p. 36, this effect rarely approaches 0.01 per cent and is generally negligible.

METHODS OF WEIGHING

1. **Weighing by Deflection and Sensibility.** The sensibility must be determined for the load in question, as has been explained on p. 45. The deflection of the empty balance is found before each series of weighings by releasing the balance beam and pans and noting an odd number of turning points after the first two:

Left Readings	Right Readings
−4.2	5.2
−3.9	4.8
−3.6	av. 5.0
av. −3.9	

The deflection for the empty balance is $5.0 - 3.9 = 1.1$. Suppose that the load is close to 20 g. and that the sensibility is 0.0002 g. per pointer division at this load. By systematic trial of weights the object has been found to be, for example, greater than 19.58 and less than 19.59 g. With the balance door closed, the rider is tried at large divisions, 9, 8, 7, etc. until it is found by releasing the beam system that the weight is greater than 19.584 and less than 19.585 g., by observing the direction and excursion of the pointer tip. The rider is placed on division 4 and the deflection is noted by taking turning points of the pointer tip:

Left Readings	Right Readings
−2.1	4.2
−1.9	4.0
−1.7	av. 4.1
av. −1.9	

The deflection is then $4.1 - 1.9 = 2.2$. The difference between the two deflections 2.2 and 1.1 times the sensibility for the load on the pans, or 0.0002 in this case, gives the weight to be added to 19.584. The weight of the object is therefore $19.584 + (2.2 - 1.1) \times 0.0002 = 19.5842$ g.

1. *a*. **Weighing by Resting-Point and Sensibility.** With damped balances, the resting-point is necessarily found because of the characteristics of the damping process. With a magnetically damped or an air damped balance a table of displacements of the resting point per milligram of excess weight on one side of the beam is found for various loads, e.g., 0, 10, 20, etc. grams in each pan. The weight corresponding to a displacement of one division on the pointer scale is then calculated (0.0010 g. divided by total displacement = gram per a displacement of 1 division). There is thus set up a table analogous to that on page 46 except that for the same balance the displacements of the point of rest per milligram are half as great as the deflections and hence the weight per pointer division and the weights per pointer division are twice as great. For the same weighing example that has been discussed in the preceding section it would be found that the weight of the object is greater than 19.584 and less than 19.585. The resting-point with the balance empty would have

been found at 0.6 and that with the balance loaded at 1.1, and the sensibility would be 0.0004 g. per division. Weight: $19.584 + (1.1 - 0.6) \times 0.0004 = 19.5842$ g.

It has been pointed out by Benedetti-Pichler (loc. cit.) that the use of resting-points instead of deflections involves the division of both the numerator and the denominator of a fraction by two in the expression for the mass to be added in the fourth place: Mass = Difference between deflections $\times \frac{1}{\text{Change in deflection per mg.}}$. The use of deflections is therefore desirable when possible. As has been stated, with a damped balance only the resting-point may be observed, since the damping action brings the pointer very rapidly to a standstill at the resting point.

The *deflection difference* is the difference between the deflection with the weights and object in place and that for the unloaded balance.

2. **Restoring the Deflection of the Empty Balance.** This method is identical with that described in (1) to the point where the weight has been found to lie between 19.584 and 19.585. By trial and error the proper tenth of a division between 4 and 5 is found to restore the original deflection determined immediately prior to the weighing.

2. a. **Short Swing Method.** In practice the method may be abbreviated to determination of the position of small approximately equal swings. These methods [2, 2 (*a*)] have the advantage that the sensibility need not be determined, but it is difficult or impossible to use them with precipitates which tend to take on moisture or carbon dioxide rapidly from the atmosphere.

3. **The Single Deflection Method.** If balances with air or magnetic damping are available this method is used. The deflection change per milligram may be found for various loads, as in method (1) or the original deflection may be restored by trying the rider in various positions, as in method (2). With other balances an excess load of 1 mg. is added to the left pan by changing the adjustment screws (t, t', Fig. 17) or by placing a 1 mg. weight on that pan. It is then possible to weigh by restoring the single deflection that occurs on releasing the pointer, or

to calibrate the deflections in terms of milligrams.[1] Brinton found that the method is not applicable to balances that have a single release mechanism for both beam and pans. Except with properly damped balances the method cannot be recommended for general use, although it is of value when the demands of speed and degree of precision permit.

Preliminary practice. This is advisable either by weighing a set of test pieces, or by a simple experiment such as that on quantitative drying as described on p. 60. If the weights are to be calibrated by one of the more accurate weighing methods that are about to be described, other preliminary practice is probably superfluous. Whenever circumstances permit it is desirable to begin with weights that have been adjusted so that the corrections are negligible, or else to supply corrections for the first term or semester of work.

METHODS BY WHICH TRUE MASSES MAY BE FOUND

The two methods that follow are used mainly in investigations and processes requiring high accuracy; in analyses the relative nature of the process, that is, the determination of parts of each substance per 100 parts of initial material, makes it unnecessary to know the absolute values of the weights, but merely their relative ones. In determining fundamental constants it is necessary to determine true masses. The calibration of weights requires the elimination of error due to inequalities of the arm lengths of the balance. Either of the following weighing methods may be used in calibrating weights or in other processes that require high accuracy.

4. **The Gauss Method of Double Weighing.** Let W be the true weight of an object, and let w be the weight found with this object on the left pan. The object is now placed on the right pan, and is found to have an apparent weight of w'. From the law of the lever: $Wl = wr$ and $w'l = Wr$, where r and l are the lengths of the right and left balance arms, respectively. By multiplication of the two relations, $W^2lr = ww'lr$, or $W^2 = ww'$ and $W = \sqrt{ww'}$. If the values of r and l are very nearly equal, as is practically always the case, the value of W may be cal-

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[1] R. R. Turner, Chemist-Analyst, 1916; P. H. M. P. Brinton, J. Am. Chem. Soc. **41**, 1151 (1919).

culated closely enough by taking the average of w and w', or $W = \frac{w + w'}{2}$.

Use of Ratio of Balance Arms. If weights of known relative values are available, the foregoing process may be used to determine the arm ratio of a balance. Suppose W is the true weight of the object, and w the value of the weights with the object in the left pan: $Wl = wr$. Now place the object on the right pan and assume $w + a$ to be the weight necessary on the left pan: $(w + a)l = Wr$. Multiply these two equations: $W(w + a)l^2 = Wwr^2$. The arm ratio is: $\frac{r}{l} = \sqrt{\frac{w + a}{w}}$. When this quantity has been determined, the object may be weighed as usual, and the weight found is multiplied by $\frac{r}{l}$ to give the true weight.

5. **Borda Substitution Method.** This method is frequently used in testing a set of weights. It is independent of the arm lengths of the balance. The object to be weighed is counterbalanced with any convenient counterpoise or tare, weights being commonly used. Then, without disturbing the counterpoise in any way, the object is removed and weights are put in place until the equilibrium against the counterpoise is restored.

Buoyant Effect of Air. This effect does not enter seriously into the work of an elementary quantitative course, except in connection with the calibration of volumetric glassware. Tables which take the effect into account are available, p. 107. The correction may be derived in the following manner: Let W_0 be the weight of an object *in vacuo,* and W its observed weight in air; then $W_0 = W + (V - V')a$, where V is the volume of the object, V' that of the weights and a is the weight of 1 ml. of air. (This value, a, at average humidity and room temperature is 0.0012 g.) In terms of weight and density, $V = \frac{W_0}{s}$, and $V' = \frac{W}{s'}$, where s and s' are the densities of object and weights respectively, in grams per ml. Since W and W_0 are so nearly equal:

$$W_0 = W + W\left(\frac{a}{s} - \frac{a}{s'}\right).$$

Thus in weighing 10 ml. of water against brass weights (density 8.4) $V - V' = 10 - 1.19 = 8.81$ ml., and the weight of this volume of air is 0.0106 g., the correction to be added.

THE CALIBRATION OF WEIGHTS

The substitution method of Richards[1] is a very good one for all purposes. This method is distinguished by the simplicity of derivation of corrections from a series of observational equations without the use of complicated algebraic formulas.[2]

Substitution Method. An extra set of analytical weights must be borrowed for use during the calibration. Note that the comparison of pieces of the same denomination must be made with the same counterpoise in place, but that the calibration may be worked at in short intervals of time, since each stage in the operation is independent of the time when the next set of comparisons is made.

The deflection of the empty balance need not be found.

If the balance has both right and left arms graduated the weights to be calibrated may be placed on the left pan. If the balance which is to be used has divisions marked only on the right side of the beam, then it is probably necessary to place the weights to be calibrated on the right side since the rider placed at division 10 will be needed to make the sum of the fractions balance a 1 g. weight. It will be assumed in the following that the set to be calibrated is placed on the right pan. It will also be assumed that the balance has a uniform sensibility of 0.00020 g. from 0. to 50 g. loads. The following procedure will serve as a guide:

Place a 0.01 g. weight from the extra set on the left pan, and a 0.01 g. weight from the set to be calibrated on the right. Determine the deflection. Now replace the right-hand weight by another 0.01 g. weight (designated as 0.01′) from the set to be calibrated, and redetermine the deflection. Repeat the observation, having the rider at division 10 on the right and no weight on that pan.

Place a 0.02 g. weight from the extra set on the left pan instead of a 0.01 g. weight. On the right place the 0.01 and 0.01′ g. weights (or 0.01 g. and rider at division 10 if only one 0.01 g. weight is in the set). Determine the deflection. Repeat with the 0.02 g. weight from the set to be calibrated in place of the two 0.01 g. weights.

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[1] T. W. Richards, J. Am. Chem. Soc. **22,** 144 (1900).

[2] F. C. Eaton, J. Am. Chem. Soc. **54,** 3261 (1932).

Repeat the operation, comparing each weight of a given denomination with the sum of the smaller weights, and with the weights of the same denomination. When this process has been completed a table of data similar to Table I, p. 57, should be prepared.

The differences in column 4 are between the first and the succeeding values for a single denomination. If the weights that are being calibrated are on the right-hand pan, a deflection more to the negative side means a heavier weight than the others of the same denomination, since a constant counterpoise is used.

The values in parentheses in column 6 are found by adding the previously determined values for the smaller weights. Since the values in this column are all relative to a small weight that was provisionally assumed to have the value marked upon it they frequently run up or run down systematically if the first weight happened not to be in relative agreement with the others. After this relative set of values has been obtained it is redistributed relative to one of the larger weights., e.g., 10, 20 or 50 g.

The redistribution might be done by calculating out individual proportions, but it is much easier to do it by taking the relative experimental value of one of the larger weights from column 6. The weights that are in relative agreement should be definite fractions or multiples of this experimental value, and hence by setting down the values as has been done in column 7, one may compare the numbers in columns 6 and 7 and it can be seen at once whether the relative experimental values are definite fractions or multiples of the larger weight that was chosen.

The corrections that are given in column 8 of the table are those to be applied to the value marked on the weight. For example the weight marked 0.2 g. is heavy and really weighs 0.2002 g. relative to the 50 g. weight taken as 50.0000; all of the 1 g. weights are heavier than $1/50$ of the 50 g. weight, whereas the 0.5 g. weight should be called 0.4999. The corrections in the sense here given are values to be added algebraically to the value marked on the weight.

If the corrections are numerous, a table may be compiled to show the total correction to be applied in any case. The table is compiled under the assumption that whenever two weights of the same denomination occur, e.g. 0.01 and 0.01′, 0.1 and 0.1′,

TABLE I. THE CALIBRATION OF A SET OF ANALYTICAL WEIGHTS. SUBSTITUTION METHOD.

1. Tare on Left Pan	2. Weight on Right Pan	3. Deflection	4. Diff. in Deflections (Col. 3)	5. Diff. (4) × Sensibility (0.0002)	6. Rel. Values if 0.01 g. Correct	7. Proportional Parts of the Value of the 50 g. in Col. 6	8. Rounded Correction to Be Applied
0.01	0.01	0.4	.....	....	0.01000	0.01005	−0.0001
....	0.01′	0.0	+0.4	+0.00008	0.01008	......	±0.0000
....	rider at 10	0.4	0.0	....	0.01000		
0.02	0.01..0.01′	−0.6	.....	....	(0.02008)		
....	0.02	−1.8	1.2	0.00024	(0.02032)	0.02010	+0.0002
0.05	0.02, 0.01, 0.01′, rider	−0.4	.....	....	(0.05040)		
....	0.05	0.2	−0.6	−0.00012	0.05028	0.05025	±0.0000
0.1	0.05 and sum	0.6	.....	....	(0.10068)		
....	0.1	1.4	−0.8	−0.00016	0.10052	0.10049	±0.0000
....	0.1′	1.4	−0.8	−0.00016	0.10052	......	±0.0000
0.2	0.1 +0.1′	0.8	.....	....	(0.20104)		
....	0.2	0.8	0.0	....	0.20104	0.20099	±0.0000
0.5	0.2, 0.1, 0.1′ and sum	−0.2	.....	....	(0.50276)		
....	0.5	+1.8	−2.0	−0.00040	0.50236	0.50247	−0.0001
1.0	0.5 and sum	0.4	.....	....	(1.00512)		
....	1	0.8	−0.4	−0.00008	1.00504	1.00495	+0.0001
....	1′	0.6	−0.2	−0.00004	1.00508	......	+0.0001
....	1″	−1.5	1.9	0.00038	1.00550	......	+0.0006
2.0	1 +1′	1.8	.....	....	(2.01012)		
....	2	2.0	−0.2	−0.00004	2.01008	2.00989	+0.0002
5	2, 1, 1′, 1″	−2.6	.....	....	(5.02570)		
....	5	1.8	−4.4	−0.00088	5.02482	5.02473	+0.0001
10	5, 2, 1, 1′, 1″	−1.4	.....	....	(10.05052)		
....	10	2.8	−4.2	−0.00084	10.04968	10.04947	+0.0002
....	10′	3.8	−5.2	−0.00104	10.04948	......	+0.0000
20	10 +10′	−0.6	.....	....	(20.09916)		
....	20	−0.8	0.2	0.00004	20.09920	20.09894	+0.0003
50	20, 10, 5, 2, 1, 1′, 1″	−2.2	.....	....	(50.21888)		
....	50	5.5	−7.7	−0 00154	50 21734	50 24734	±0.0000

1.1′ and 1.1″, the unprimed or lower primed weights will be used in any weighing not requiring the use of all of them.

Gauss or Double Weighing Method of Calibration. It has been pointed out by Weatherill[1] that the Gauss double or transposition method, when used in the calibration of weights, enables one to obtain approximately double the accuracy in the comparison of weights. A further advantage is that no extra set of weights is needed.

The procedure at any stage of the comparison is as follows: Assume W_1 and W_2 to be weights of the same denomination which are to be compared. W_1 is placed on the left pan and W_2 on the right, and the deflection is found. The position of the weights is now reversed and the deflection is redetermined. With a known sensibility the value of one weight in terms of the other may be found, assuming the two arms of the balance to be equal. For the first position, $W_1 = W_2 + w$, and for the second position $W_2 = W_1 + w'$ where w, w' may be positive, negative or zero. Subtracting, $W_1 - W_2 = W_2 - W_1 + (w - w')$

and $2W_2 = 2W_1 - (w - w')$ or $W_2 = W_1 - \frac{(w - w')}{2}$

But $w = (\text{defl}_1 - \text{defl}_0) \times \text{Sensibility}$, and $w' = (\text{defl}_2 - \text{defl}_0) \times \text{Sensibility}$, where defl_0 is the deflection of the empty balance, which need not be determined since it cancels out.

$$W_2 = W_1 - \frac{(\text{defl}_1 - \text{defl}_2) \times \text{Sens.}}{2}$$

or

$$W_2 = W_1 + \frac{(\text{defl}_2 - \text{defl}_1) \times \text{Sens.}}{2}$$

If a balance has a beam that is graduated on both sides no extra weight will need to be borrowed; if the graduations are only on the right an extra 0.01 g. weight will need to be borrowed. The manner of tabulating and working up the data are indicated in Table II. The redistribution of the provisional values, column 6, and the determination of the corrections are done as in the preceding method, p. 55.

The values in column 7 are obtained by dividing the value for the 50 g. weight (50.02760) obtained, column 6, by $\frac{5}{2}$, 5, 10,

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[1] P. F. Weatherill, J. Am. Chem. Soc. **52**, 1938 (1930).

TABLE II. CALIBRATION OF WEIGHTS. TRANSPOSITION METHOD

1. Wt. First Placed on Left Pan	2. Wt. First Placed on Right Pan	3. Defl$_1$	4. Defl$_2$ (After Transpos.)	5. ½ (Defl$_2$ − Defl$_1$) × Sensibility (0.00020)	6. Values Relative to 0.01 g. Wt.	7. Fractions of Value for 50 g. Wt. (Col. 6)	8. Corrections, Rounded to Fourth Place, to Apply to Value Marked on Weights
0.01					0.01000		
....	0.01′	−0.4	0.4	0.00008	0.01008	0.01006	....
....	0.01″	−0.4	−0.4	....	0.01000	....	−0.0001
0.01, 0.01′					(0.02008)		
....	0.02	1.2	−0.4	−0.00016	0.01992	0.02001	−0.0001
0.02, 0.01, 0.01′, 0.01″					(0.05000)		
....	0.05	−0.8	−0.4	0.00004	0.05004	0.05003	....
0.05, 0.02, 0.01, 0.01′, 0.01″					(0.10004)		
....	0.1	−1.2	0.4	0.00016	0.10020	0.10006	0.0001
....	0.1′	0.4	−0.8	−0.00012	0.09992	....	−0.0001
0.1, 0.1′					(0.20012)		
....	0.2	−0.4	1.0	0.00014	0.20011	....	0.0003
0.2, 0.1, 0.1′, etc.					(0.50042)		
....	0.5	1.2	−0.6	−0.00018	0.50024	0.50028	....
0.5, 0.2, etc.					1.00066		
....	1	1.0	−1.6	−0.00026	1.00040	1.00055	−0.0002
....	1′	1.6	0.4	−0.00012	1.00054	....	....
....	1″	0.6	0.4	−0.00002	1.00064	....	0.0001
1, 1′					(2.00094)		
....	2	−1.2	0.8	0.00020	2.00114	2.00110	....
2, 1, 1′, 1″					(5.00272)		
....	5	1.6	2.4	0.00008	5.00280	5.00276	....
5, 2, 1, 1′, 1″					(10.00552)		
....	10	0.0	−0.4	−0.00004	10.00548	10.00552	....
....	10′	−0.6	0.4	0.00010	10.00562	....	0.0001
10, 10′					(20.01110)		
....	20	−2.0	−1.2	0.00008	20.01118	20.01104	0.0001
20, 10, etc.					(50.02780)		
....	50	0.6	−1.4	−0.00020	50.02760	50.02760	Standard

25, 50, etc. These values (column 7) are then compared with the relative values in column 6 for the various weights to obtain the corrections, rounded in the fourth place in column 8. The corrections when added algebraically to the values marked on the weights give the relative masses of the weights.

AN EXPERIMENT IN QUANTITATIVE DRYING

Determination of Water in a Hydrated Salt or Other Material.

The loss in weight that a substance undergoes at 100–105° C. represents moisture that is bound superficially for many inorganic substances. Certain hydrated salts lose all or a definite portion of their molecules of water of crystallization at this temperature.

Two marked crucibles and lids are heated until the marks have been burned in as described on p. 12. The crucibles are cooled in a desiccator to balance temperature and weighed. About a gram of the powdered[1] and well mixed material is weighed accurately from a weighing bottle by the method of difference as described on p. 47. In this case the material is transferred directly to the weighed crucible over clean paper, preferably glazed so that there is an opportunity to detect mechanical loss and to recover material quantitatively if any is spilled. The weighing bottle is reweighed, and a second sample of about a gram is placed in the second crucible; the bottle is reweighed. With nearly all powdered substances it is futile to attempt to check the weight of the sample by reweighing the crucible plus the sample.

Each crucible with its lid beside it is placed in the smallest beaker which will accommodate it, covered with a watch glass supported on glass hooks and heated for two hours or over night in an oven regulated at 100–105° C. The crucibles and their lids are then transferred to a desiccator, cooled and reweighed. The crucibles are reheated for one hour or more, cooled, and weighed. The heating, cooling and weighing are repeated until the weight does not vary by more than 0.0002 g. The percentage loss in weight is calculated and reported as water lost.

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[1] If the material is a hydrated salt in rather large crystals it is broken down to a coarse powder with particles about 0.5 mm. rather than to a fine powder to avoid loss of water during the powdering operation.

The data should be entered in the notebook in an orderly fashion, as for example:

Determination of Per Cent of Water Lost by a Crystalline Substance.

	1.	2.	
Weight of weighing bottle and salt	11.6524	10.5495	Date ......
Weight of weighing bottle less sample	10.5495	9.5561	
Weight of sample	1.1029	0.9934	
Weight of crucible and lid	19.7832	21.2455	
Weight of system before heating	20.8861	22.2389	
Weight after heating over night	20.7168	22.0881	Date ......
Weight after heating 2 hours longer ..	20.7166	22.0877	Date ......
Weight after heating 2 hours longer ..		22.0876	Date ......
Weight of water lost	0.1695	0.1513	
Per Cent of Water	15.37	15.23	Date ...... Completed

(The weights and corrections, method of calculation or any other relevant data should be recorded in the notebook, for example, on the left-hand pages. Some investigators prefer to enter all data on the right and to make frequent summaries of the results for individual determinations and for complete analyses. In some laboratories, both educational and industrial, there are rigid requirements about the form in which the record is to be kept. Attention should be given to the system recommended.)

Review Questions and Problems

1. The density of aluminum is 2.6 and that of bronze is 8.5. What relative lengths of beams of these materials would give balances of the same general performance, friction being assumed negligible and the beams assumed to be of the same uniform cross-section?

2. A 20 g. platinum crucible and a nickel crucible exactly balance each other in air on an equal-arm balance. What is the difference in weight between them in vacuo? The density of platinum is 21.45; that of nickel 8.90. Which crucible is heavier in vacuo?

3. A balance with 6 divisions from fulcrum to terminal knife edge is equipped with a 10 mg. rider. With the rider at division 4 what error would be made if the rider were assumed to be correct for the balance without testing?

4. A 1.0000 g. sample yields 0.1650 g. of a pure oxide weighed in air against brass weights. Taking the densities of the sample as 2.4; of the oxide as 7.6 and of the weights as 8.4, calculate the percentage of oxide in vacuo and in air.

5. Ten milliliters of water of density approximately 1 are weighed with brass weights, density 8.4 in air. The weight found is 9.972 g. Calculate what the weight of the water would be in vacuo.

6. May an analytical balance be used to obtain true masses if the ratio of the two lever arms is not determined?

7. When a set of weights is calibrated for analytical work is it essential to include a weight certified by the U. S. Bureau of Standards in the calibration? Reasons.

8. A weighing bottle containing 3 ml. of air is stoppered while at 100° C. and 760 mm. pressure and remains airtight until after it is weighed at 20° C. Calculate the error due to the fact that the air in the vessel is not at atmospheric pressure.

9. Given a balance of sensibility of 0.00020 g./div. what maximum and minimum errors in weighing will result if the average turning points, both left and right for both deflections, are subject to an error of 0.2 division each? Ans. Max. 0.00016; min. 0.

10. A glass vessel is calibrated by weighing it empty, then filled with mercury, using brass weights. If 159.65 g. of mercury are found in air against brass weights, what error is made by neglecting a vacuum correction? (Density of mercury 13.59; weights 8.4.) Ans. The volume found is too large by 0.00065 ml. in a total volume of 11.747 ml.

CHAPTER IV

SCIENTIFIC MEASUREMENTS

ACCURACY; PRECISION; ERRORS; COMPUTATION

The measurements that are made in quantitative analyses illustrate the general characteristics of all scientific observation. The goal is to establish quantitatively certain scientific facts which are frequently accurate measurements expressed numerically in suitable units and to the proper number of figures in view of the errors that are involved.

Accuracy as used in connection with scientific facts means the closeness of approach of a measurement or of a series of similar measurements to the true value of the quantity measured. Since there is no absolute way of measuring any physical quantity, the truth is taken as the most probable value from the available data, critically considered for sources of error. Our confidence is increased if different observers using independent methods arrive at experimental values for a constant that agree to an extent estimated to be within the probable limits permitted by the methods. The mathematical theory of probability is very important in devising checks and balances which enable one to investigate the results of observations critically and to decide, for example, whether an apparent trend is significant or merely a chance affair within the limits of the errors of measurement.

Precision means the closeness of approach of a number of similar measurements to a common value. Precision is very desirable but the attainment of precision is not in itself proof that an accurate series of measurements has been made. The reason for this is that constant sources of error may enter into all of the measurements in the series. For our purposes precision is measured in terms of deviations of the individual measurements of a series from the average value of that series. The deviations, regardless of sign, are best expressed in quantitative analysis in parts per 1000 parts of the quantity dealt with or measured.

Deviations in parts per 1000 are calculated by proportion from the data. Example: In a series of volumetric standardizations the following values for the normality of a solution were found:

	Normality	*Individual deviations from the average*	*Deviations, parts per 1000 parts* *
(1)	0.0976	0.00002	0.2
(2)	0.0974	0.00018	1.8
(3)	0.0977	0.00012	1.2
(4)	0.0976	0.00002	0.2
	Av. 0.0975_8 †	Av. 0.000085	Av. 0.85

This illustration represents the normal degree of precision to be attained by proper use of the volumetric equipment. The average value, 0.0976 might be relatively far from the truth if all of the individual determinations were affected to the same extent by a source of error. When one follows a good procedure, that has been adequately studied, with suitable equipment and proper skill there is a very strong probability that precise measurements will also be accurate.

Errors. An error in a measurement is the difference between the observed value and the true value of the quantity measured. The latter, when established experimentally, can only be known within certain probable limits. Errors are of two general classes: (*a*) Determinate or systematic, and (*b*) Indeterminate. The determinate errors may be discovered, and corrected for or eliminated.

(*a*) **Determinate Errors.** The chief kinds of errors in this classification are:

(*i*) *Personal Errors.* These are due to factors for which the experimenter is responsible. In analysis some common types are neglect of the use of a proper reading device on a buret; inability to perceive certain color changes that occur in work with indi-

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* Calculated as follows: $\frac{0.00002}{0.09758} = \frac{x}{1000}$

† The value 0.0975_8 is carried out one place further than the data justify for use in the intermediate stages of the calculations. The dropping of the number 8 below the line of the other numbers is to indicate this. A rounded value of 0.0976 would be used in analyses.

cators; failure to make volumetric solutions homogeneous; erratic reading of pointer swings at the balance or of values marked on the small weights.

(*ii*) *Instrumental Errors.* As the name implies these are due to the instruments. Imperfect weights, volumetric glassware and balances are sources of error that are easily discovered by simple tests. If the weights must be known in terms of their true masses a suitable weight may be sent to the National Bureau of Standards and received again with certificate of mass at moderate cost; this weight then serves as a basis for calibrating local sets.

(*iii*) *Errors in Method.* In this class belong errors due to such factors as the solubility of a precipitate in the solution with which it is washed; the use of an inadequate temperature during the drying and final heating of a precipitate; neglect of an indicator correction in certain types of volumetric work, etc.

There is continual effort to modify methods in the direction of greater accuracy, combined where possible with increased convenience and speed. Inadequate methods are replaced as soon as possible by others different in principle or type. In research of a critical nature upon unfamiliar or new procedures variations are tested by applying them to analyzed samples of appropriate type obtainable from the National Bureau of Standards. The certified values for these samples are obtained by taking averages weighted according to number of parallel determinations, method used, etc., of the average results submitted by a number of skilled analysts at the Bureau and in industrial or university laboratories.

After the determinate errors have been eliminated, estimated or otherwise accounted for, there always remain slight variations between successive values obtained by the same method; these errors are indeterminate ones.

Indeterminate Errors. The cause of these errors is probably slight variations in judging phenomena or slight variations in the performance of the instruments. Errors of this sort have been found to have a probability distribution that may be expressed mathematically as follows:

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

where y is the frequency of occurrence of a deviation.

h is a constant characteristic of one kind of measurement, but different for different kinds.

x is the magnitude of a deviation of frequency y.

e is the base of the natural logarithmic system and π has its usual significance.

A graph of a large number of observations with frequencies of occurrence of deviations (y) as ordinates and the magnitudes of the deviations as abscissas has the form shown in Fig. 25. A very large number of observations is needed for a close approach to the true value which then lies between the positive and negative values of the average deviation. Since positive and negative values for the deviations occur with equal frequency, the best choice to make is the arithmetical mean.

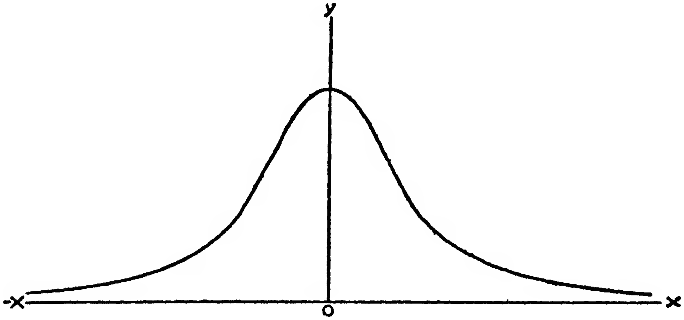

Fig. 25. The Distribution of Experimental Errors. The ordinates, y, represent the frequencies of occurrence of errors of magnitudes, x.

The average deviation of an individual measurement from the arithmetic mean has been mentioned as a measure of precision p. 63. The arithmetic mean of a brief series of measurements is a much less reliable approach to the truth than the mean of a more extended series of measurements, and it has been found that reliability of the arithmetic mean increases in proportion to the square root of the number of parallel measurements, other things being equal. The mean of nine similar measurements should be 3 times as reliable as a single measurement or $1\frac{1}{2}$ times as reliable as four parallel measurements.

There are several ways of treating the data from an extended series of measurements. For example, the mean error of a single measurement is:

$$\text{Mean error of individ. meas.} = \sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + d_n^2}{n}}$$

The probable error of a single measurement is:

$$\text{Probable error, individ. meas.} = 0.67\sqrt{\frac{d_1^2 + d_2^2 + d_3^2 + \cdots d_n^2}{n - 1}}$$

In these expressions, d_1, d_2, etc., are the deviations of individual values from the arithmetic mean and n is the number of measurements. The expression "Probable Error" as used here has a technical significance and means that in a very long series of measurements influenced by indeterminate errors the number of measurements having an error larger than the probable error will be equal to the number having a smaller error. There are still other ways of treating the errors in an extended series of measurements, but there is little or no occasion for the student to use them in connection with a course in quantitative analysis.[1]

Rejection of Observations. In principle no result should be rejected except for a clearly known source of error. Measurements that deviate widely from the mean in a long series are frequently omitted in striking an average, with discussion of the reasons for omission. The occurrence of one rather divergent value in a series of four parallel estimations without apparent cause is of rather common occurrence, especially while one is mastering the technique of quantitative analysis. Mellor (loc. cit.) states that one will be correct 99.3 per cent of the time in rejecting a divergent value if its deviation from the average of the three other determinations is greater than four times the

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[1] References. A. deF. Palmer, The Theory of Measurements, McGraw-Hill. J. W. Mellor, Higher Mathematics for Students of Chemistry and Physics, Longmans Green & Co. Chemical Computations and Errors, T. B. Crumpler and J. H. Yoe, J. Wiley & Sons, Inc., 1940. Brief reviews of the various ways of treating errors of measurement will be found in H. A. Fales and F. Kenny, Inorganic Quantitative Analysis, D. Appleton-Century Co.; I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Inorganic Analysis, Macmillan Co.

average deviation of these three. Illustration: The following percentages were found in analyzing a given material:

(1) (2) (3) (4)
10.12, 10.41, 10.25, 10.17. Averaging the more concordant determinations, (1, 3, 4):

	Values	*Deviations*
	10.12	0.06
	10.25	0.07
	10.17	0.01
Av.	10.18	Av. 0.05

The deviation of the suspected result, 10.41 per cent, is 0.23 from the average of the others and 0.23 is more than four times 0.05, the average deviation of the other results, and the suspected result may be rejected with a 993/1000 chance of being justified, according to the rule. There is no rule for the selection of values when less than four measurements of the same quantity have been made. Practice is essential to the development of skill in analytical work as well as in any other specialized technique.

A distinction should be made between *absolute* errors and *relative* errors. For example an inherent error of 0.002 g. may occur in a method regardless of the amount of the initial sample between rather wide limits. This would be called an absolute error. An error of 0.002 g. would of course be a rather large error of 2 per cent if the initial sample were 0.1000 g., whereas it would be a rather minor error of 0.2 per cent if the initial sample weighed 1.0000 g. For a constant weight of sample it is progressively more difficult to obtain acceptable results as the percentage of the constituent sought approaches 100 per cent of the sample; the larger the absolute error of the method the greater is the difficulty. A loss due to the solubility of a precipitate is an example of an absolute error under standardized conditions.

A *relative* error is one which is independent of the weight of the sample. For example a given kind of precipitate may always adsorb one per cent of another substance, and hence weigh one per cent more than it should regardless of the weight of the initial sample.

For the reasons given above it is preferable in reporting the results of a new analytical method to express the error in milligrams.

The Rules of Observation and Computation. The carrying of unnecessary figures through the record is to be avoided. The principle is to retain in a measurement only *one* uncertain figure. The uncertain figure occurs as the result of an estimate between divisions marked on a scale, for example on the scale against which the position of the pointer of a balance is read, or a buret which is calibrated only as far as tenths of milliliters. Weights in grams are recorded with four figures to the right of the decimal point with a balance suitable for macro-scale weighings, for example 10.4563 g. Buret readings are estimated to the nearest hundredth, e.g., 44.56 ml. Sometimes an extra figure is carried through the intermediate stages in a calculation, especially if upon averaging a 5 is obtained in the first place beyond the proper number of figures. The final result is rounded off to the proper number of significant figures.

Significant Figures. If we follow the rule that only one uncertain figure is retained in recording a measurement, the digits thus set down are significant figures. Zero, however, may be used either as a significant figure or as an indication of order of magnitude. Illustration: In a weight such as 0.2050 g. the zero to the left of the decimal point is not a significant figure, but merely indicates that the weight is less than one gram; the other two zeros are significant figures. One thousandth of the equivalent weight of hydrogen is 0.001008 g. (milliequivalent weight). The zero to the left and the first two zeros to the right of the decimal point are not significant figures, but serve to indicate the order of magnitude of the quantity. The two zeros between the 1 and the 8 are significant figures. In the buret reading 40.06 ml. both of the zeros are significant figures. In a number like 3.14×10^{-5} or 8.92×10^{6} there are three significant figures in the measurement and the 10^{-5} or 10^{6} indicates the order of magnitude.

Computations. In rounding off observed or computed quantities to the proper number of significant figures, 1 should be added to the last significant figure if the figure in the next position is equal to or greater than 5. For example, the weighing:

$10.974 + (1.8 \times 0.00020) = 10.97436$ g. would be rounded to 10.9744 g.

Addition or Subtraction. In a sum or difference the figures should be retained to that point farthest to the right, relative to the decimal point, in which an uncertain figure occurs in any of the numbers to be added or subtracted, after rounding them off as described in the preceding section. Illustration: To add 72.95, 1.052 and 5.436:

$$\begin{array}{r} 72.95 \\ 1.05 \\ 5.44 \\ \hline 79.44 \end{array}$$

Multiplication and Division. In general a product or a quotient should contain as many significant figures as there are in that factor which has the least number of significant figures. A product or a quotient can have no greater percentage certainty than that factor in the process which has the least percentage certainty. Example: To multiply $0.3621 \times 1.4 \times 0.228$. The result is 0.12. In many of the analytical determinations all of the data have four significant figures and hence the result is in general expressed to four significant figures, at most. If a small weight of some substance is obtained, e.g., 0.0455 g. from a one gram sample, then only three significant figures are retained in the result.

The Accuracy to be Expected. It is impossible to give any brief general statement that will cover the question of the accuracy to be expected in a first course in quantitative analysis. It varies with the equipment, the substances analyzed, the relative proportions of the substances present, the size of the sample, the method, the objectives of the course, etc. With equipment of the kind commonly provided it is possible to attain an accuracy within 2 parts per 1000 parts of substance handled in volumetric standardizations, and in certain analyses. In simple volumetric and gravimetric estimations, when the initial samples weighed are of the order of 1 gram, duplicate determinations of substances present in substantial amounts, for example 10 per cent up may be expected to agree within 2 parts per 1000 parts of the initial sample. Considering a 1.0000 g. sample, an error of 2 parts per

1000 parts is 2 milligrams. Expressed in terms of the substance estimated, this error would correspond to 0.2 in the figure found for the percentage; that is, duplicate values such as 30.5 and 30.7 per cent of substance found would be regarded as in good agreement. It is better to consider the precision and accuracy to be expected in the light of local objectives; two parts per 1000 probably represents the upper limit of accuracy that is generally provided for in a first quantitative course.

Aids to Computation. A ten-inch slide rule is very useful for approximate calculations, but does not enable one to attain sufficient precision in many instances. Therefore a five-place logarithm table has been included in the Appendix, to be used in calculating the results that are to be reported. A brief explanation of the use of logarithms is given in the section of the Appendix which precedes the table. There is also given there an explanation of the principles of dealing with very large or very small numbers in the form of exponents of the base 10, i.e., in logarithmic form.

Review Questions and Problems

1. Criticize the statement: "The absolute value of the electrochemical equivalent of silver is 0.001118 g. per ampere per second."

2. How many significant figures are there in each of the following: (a) An ionization constant, 0.00126; (b) A weight, 10.9506 g.; (c) Avogadro's number 6.06×10^{23}; (d) In the constant 6.1×10^{-5}; (e) In the molecular weight of calcium carbonate, 100.09? Ans. (a) 3; (b) 6; (c) 3; (d) 2; (e) 5.

3. Calcium carbonate contains 56.04 per cent of lime. Calculate the weight of lime, to the proper number of significant figures, in 20 pounds of calcite, a pure form of calcium carbonate. Ans. 11. lbs.

4. A 1.0456 g. sample of a hydrate lost 0.0268 g. upon heating. Calculate the per cent of weight lost to the proper number of significant figures. Ans. 2.56.

5. Four measurements of the normality of a solution were (a) 0.1470; (b) 0.1467; (c) 0.1465 and (d) 0.1469. Calculate the deviations in parts per thousand and decide whether any of the results should be rejected according to the rule.

6. Find to the proper number of significant figures:
   (a) The product of $107.88 \times 0.001118 \times 3600$.
   (b) The quotient of 10.36854 divided by 0.2474.
   (c) The sum of 2×107.88 plus 96.0 plus 4×16.0000 (molecular weight of silver molybdate).

CHAPTER V

FUNDAMENTAL LAWS AND THEORIES

In quantitative analysis it is assumed that the student has a working knowledge of the calculations that are based upon the laws of conservation of mass, combining weights, definite proportions and multiple proportions. The calculations of volumetric analysis involve a knowledge of the concept of equivalent weights if the normal system is used in the preparation of the standard solutions. See pp. 93-97. Detailed illustrations of the types of calculation that are most useful in quantitative analysis will be found in Chapters VIII, IX, XI and XV.

Isotopes; Atomic Weights. Progress has been so rapid in the immediate past both in the preparation of radioactive isotopes by bombardment of ordinary material with particles of high kinetic energy, and in the separation of the naturally occurring isotopes of hydrogen (1, 2), chlorine (35, 37), carbon (12, 13), etc., that the question might arise as to whether this situation has modified the validity of the use of atomic weights, many of which are obviously numbers reflecting the composition of an isotopic mixture. It appears that except in association with radioactive natural sources or as a result of artificial transmutations or separations one is not apt to encounter unusual isotopic mixtures. Hence in the analysis of the vast majority of substances no consideration need be given to the probable occurrence of the elements in unusual isotopic ratios. The separation and utilization of pure or partially purified isotopes is a rapidly expanding field of research. The analytical methods may be conventional ones in favorable circumstances; more frequently, when the amount of material is scanty or the extent of replacement of one isotope by another is small, it is necessary to use physico-chemical methods of which the radioactive technique, where applicable, the mass spectrographic method, interferometry, density measurement and the thermal conductance method have been successfully applied.

Atomic Weights. In principle one might analyze substances for the percentages of the elements present without knowledge of atomic weights, provided a feasible scheme for the complete separation of each element from the others and a method for its quantitative recovery could be worked out. The majority of the elements are so active that this mode of procedure would be impractical in most cases or virtually impossible for certain elements, e.g., fluorine. Hence great importance attaches to the correct relative values of the atomic weights of the elements as they occur with normal isotopic distribution. These values are subject to frequent redetermination, or "revision," and to critical examination by independent methods, as for example the application of the mass spectrograph.

The chemical determination of atomic weights is in a sense the most refined type of a chemical analysis. For most of the elements the process has consisted first, in the preparation of a pure halide of the element in question, and of pure silver. All operations are made with the utmost care sparing neither time, effort nor expense. The amount of silver that combines with the halide present in a known weight of the pure halide of the element is then determined repeatedly, using rather large samples, e.g., of the order of 10 g., in each experiment. In principle the process is like that of determining halide with silver nitrate, p. 317.

The importance of correct atomic weights to the analyst is that one may separate a pure compound of the element and weigh it, rather than the element itself; the weight of the element recovered is then determined by calculation. This process not only avoids the separation and recovery of the more active elements, but also gives one "leverage" in determining the elements because they may be weighed in the form of compounds in which their percentage is low. An extreme illustration is that sodium may be weighed in the form of one of its hydrated triple salts, $NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6.5H_2O$, containing only 1.53 per cent of sodium. In volumetric analysis the possession of correct atomic weights offers corresponding advantages; for example, compounds of high equivalent weight may be used in standardizing solutions, with gain in accuracy.

Chemical Equilibrium

In analytical chemistry especial importance attaches to reactions which proceed rapidly to an equilibrium that is very far toward completion in a given direction. At present the majority of the analytical reactions are carried out in aqueous solutions; it will be necessary therefore to give special attention to the factors which affect these equilibria.

The Law of Mass Action. The first clear statement of the effect of the relative proportions of the reactants upon the completeness of a reaction was given by Guldberg and Waage[1] in the fundamental principle which we now call the *law of mass action: The rate of a chemical reaction is proportional to the active masses of the reacting substances.* In terms of this principle, every reaction that has reached equilibrium is made up of two opposed reactions still proceeding at equal speeds at equilibrium. The temperature must be constant while the relationships are being studied because of its marked effect upon reaction velocities. For a reversible reaction symbolized by: $A + B \rightleftharpoons C + D$ the speeds are $s_1 = k_1(A)(B)$ and $s_2 = k_2\ (C)(D)$, k_1 and k_2 being constants peculiar to the opposed processes and (A), (B), etc., indicating the active masses of the various substances. At equilibrium, $s_1 = s_2$, and hence $k_1(A)(B) = k_2\ (C)(D)$,

or
$$\frac{(C)(D)}{(A)(B)} = \frac{k_1}{k_2} = K \text{ (temp. const.)}$$

K is the *equilibrium constant* of the reaction at the temperature in question. Guldberg and Waage used molecular concentrations as the active masses.

Equilibrium Constants. These constants which may be derived kinetically as has been indicated, may also be derived thermodynamically in a manner that is independent of views as to mechanism, as was shown by van't Hoff.[2] When the constant has been determined it embodies much of the fundamental information about a reaction, but gives no idea as to the rate with which equilibrium is established. The original thermodynamic

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[1] C. M. Guldberg and P. Waage, Etudies sur les affinities chimiques, 1967. J. prakt. Chem. (2), **19**, 69 (1879).

[2] J. H. van't Hoff, Z. physik. Chem. **1**, 481 (1887).

derivation applied only to ideally dilute solutions or to ideal gases, since the active masses were expressed in molecular concentrations, or in partial pressures of the gases in a mixture.

An illustration of the experimental derivation of an equilibrium constant and of the effect of active masses, taken from the work of Guldberg and Waage follows:

Illustration. The transposition of barium sulfate by sodium carbonate solution. Reaction: $BaSO_4$ (solid) + Na_2CO_3 (solution) $\rightleftharpoons$ $BaCO_3$ (solid) + Na_2SO_4 (solution). The active masses of the solids are assumed to be constant, and hence the equilibrium expression simplifies to $\frac{[Na_2SO_4]}{[Na_2CO_3]} = K$. The square brackets indicate that the quantities within them shall be expressed in molecular concentrations. Guldberg and Waage found a rounded value of 0.200 for K. Their data, rearranged, is given in Table III.

TABLE III. DATA FOR THE REACTION OF BARIUM SULFATE AND SODIUM CARBONATE.[1]

Moles of Substances Originally Present		Moles of Sodium Sulfate Formed		Equilibrium Constant K
Na_2SO_4	Na_2CO_3	Observed	Calculated $K = 0.200$	
1. 0.0	5.0	0.837	0.833	0.201
2. 0.0	3.5	0.605	0.583	0.209
3. 0.0	2.0	0.337	0.333	0.203
4. 0.0	1.0	0.157	0.167	0.184
5. 0.2956	3.0	0.234	0.254	0.192
6. 0.2956	3.86	0.438	0.397	0.214

This is an unfavorable case, since the molecular concentrations of the salts are used as active masses, and as will be shown later, it is difficult to derive a correct expression for the active masses of highly ionized salts present at high concentrations.

The use of an equilibrium constant may be illustrated by checking the calculation of the third value (0.333) in the table.

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[1] From Guldberg and Waage, J. prakt. Chem. (2), **19**, 69 (1879); temperature not stated.

Let x equal the moles of sodium sulfate formed; the final concentration of the sodium carbonate will then be $2.0 - x$, and hence

$$\frac{x}{2.0 - x} = 0.200;\ 1.2x = 0.4;\ x = 0.333.$$

Determinations Nos. 1-4 of the table show the rapid diminution of the amount of transposition as the molecular concentration of the sodium carbonate is decreased; determinations Nos. 5 and 6 show the inhibiting effect of sodium sulfate, one of the products of the reaction (compare Nos. 2 and 6). In qualitative analysis a large excess of sodium carbonate should be used when this reagent is applied to the extraction of anions from insoluble salts. In quantitative work insoluble sulfates are fused with a large excess of dry sodium carbonate, a more effective procedure than the use of an aqueous solution because of the effect of temperature and concentration upon the equilibrium.

In formulating the equilibrium constant for a reaction of the type: $2A + B \rightleftharpoons C + D$, the process may be regarded as $A + A + B \rightleftharpoons C + D$, and the equilibrium expression is:

$$\frac{[C]\,[D]}{[A]\,[A]\,[B]} = \frac{[C]\,[D]}{[A]^2\,[B]} = K.$$

In general, the concentration of each reactant is raised to a power that is equal to the coefficient by which the molecular formula of that reactant is multiplied in the correct molecular equation for the reaction.

The equilibrium constant for the general reaction:

$$n_1A_1 + n_2A_2 + n_3A_3 + \cdots \rightleftharpoons n_1'A_1' + n_2'A_2' + n_3'A_3' + \cdots$$

is formulated:

$$\frac{[A_1']^{n_1'}\,[A_2']^{n_2'}\,[A_3']^{n_3'}\cdots}{[A_1]^{n_1}\,[A_2]^{n_2}\,[A_3]^{n_3}\cdots} = K.$$

For the reaction: $MnO_4^- + 8H^+ + 5Fe^{++} \rightleftharpoons Mn^{++} + 5Fe^{+++} + 4H_2O$, an equilibrium expression:

$$\frac{[Mn^{++}]\,[Fe^{+++}]^5\,[H_2O]^4}{[MnO_4^-]\,[H^+]^8\,[Fe^{++}]^5} = K,$$

would be expected to apply.

Variables Which Affect Equilibria. The chief factors which are of importance are. 1. Temperature; 2. Pressure; 3. Concentrations of the reactants; 4. Specific chemical nature of the reacting substances.

The effect of increase in temperature is to displace an equilibrium in the direction in which heat is absorbed. This is van't Hoff's principle of mobile equilibrium. If, for example, heat is absorbed as the last small quantities of a substance dissolve to form a saturated solution, increase in temperature will increase the solubility of the salt.

The effect of pressure upon an equilibrium may be predicted from the LeChatelier-Braun principle, namely that the alteration of any of the factors which determine an equilibrium will cause alteration of the equilibrium in such a way as to annul the effect of the altering agency. If gases combine with diminution in volume, then application of pressure will result in a more complete reaction, other things being equal. The effect of pressure is used to advantage in the treatment of solutions with hydrogen sulfide; also in certain of the operations of gas analysis.

The effect of concentration of reactants is one of the most valuable aids in analytical processes. Precipitations are always made more complete by using a slight excess of the precipitating reagent. Other reactions are driven to completion by removal of a gaseous product, e.g., carbon dioxide from carbonates, or by volatilizing a product of a reaction, as for example the removal of fluoride from a solution by distilling it in the form of hydrofluosilicic acid. Complex-formation is also utilized to force a reaction in a desired direction.

If a system is in equilibrium, and if the equilibrium constant is known, it is possible to derive the theoretical accuracy of an analytical process which is based on such an equilibrium. For example, the theoretical possibilities of utilizing such methods as volumetric neutralizations, precipitations or oxidation-reduction processes may be derived readily if the appropriate equilibrium constants are known.

Although the equilibrium constant may be favorable for a sufficiently complete reaction in one direction, it should always be remembered that the rate of reaction may be disappointingly slow because of a slow intermediate "rate-determining" step about which the constant gives no indication. In some cases alteration of the variables pressure, temperature and concentration, the latter by use of excess of reagent or removal of a product, will have little effect. In such instances a search for a suitable catalyst is indicated. There are very numerous instances of the successful application of catalysts in volumetric oxidation-reduction processes.

Illustrations: The presence of a silver salt catalyzes the oxidation of manganous to permanganate ion by persulfate ion. A trace of molybdate catalyzes the liberation of iodine from an iodide by hydrogen peroxide, in an acidified solution. A trace of iodide catalyzes the oxidation of an arsenite by potassium permanganate. Manganous ion catalyzes the oxidation of oxalate ion by permanganate; the reaction between oxalate and permanganate ions is therefore autocatalytic since manganous ion is one of the products of the reaction. Iodine monochloride catalyzes a large number of oxidation-reduction reactions.

The Mass Law in Terms of Activities. The active mass of a substance can be assumed to be equal to its molecular concentration under ideal limiting conditions, for example for a perfect gas at a low partial pressure or for extremely dilute solutions of non-electrolytes; for concentrated systems such as compressed gases, concentrated solutions of non-electrolytes and for dilute solutions of highly ionized substances the relation between molecular concentration and active mass has to be discovered experimentally or theoretically.

Experimentally the problem may be solved by measurements of solubility, vapor pressure lowering, electromotive force, etc., by carrying the measurements to extreme dilutions. For electrolytes the activity may be related theoretically to the charges of the ions and the dielectric constant of the medium. The detailed discussion of these methods is to be found in reference works on physical chemistry and electrochemistry. Some of the conclusions that are of interest in connection with ionic equilibria are to be found in the next section, p. 79.

If we regard the law of mass action as being universally true in terms of activities, the equilibrium constant for a reaction: $A + B \rightleftharpoons C + D$ would be written:

$$\frac{a_C a_D}{a_A a_B} = K.$$

The symbols a_A, a_B, etc., denote the activities or true active masses of the substances in question. The relation between activity and molecular concentration is then given by:

$$a_A = c_A f_A;\ a_B = c_B f_B,\ \text{etc.},$$

where c denotes molecular concentration and f the activity coefficient.

Much of the theoretical discussion in subsequent chapters rests necessarily upon equilibrium constants, especially those applicable to equilibria between ions. The use of molecular concentrations is valid only in limiting cases, but these cases are the ones of principal importance in the theory of analytical chemistry. In limiting cases the activity coefficient is equal to 1, and hence molecular concentrations may be used as active masses. Where necessary, activity coefficients may be used; these may be closely approximated from published data or by calculation (vide infra).

Ionization; Ionic Equilibria. The use of molecular concentrations as active masses applies to a good degree of accuracy over a large range of concentration for the equilibria between slightly ionized substances and their ions. The slightly ionized substances in aqueous solutions include the majority of the organic acids, not, however, the sulfonic acids; certain inorganic acids, e.g., boric, carbonic, etc.; most of the organic bases except tetramethyl ammonium hydroxide and other compounds of the same type; ammonia and hydrazine; a few salts, e.g., lead acetate; mercuric salts. See Table XXI, Appendix, for the ionization of acids and bases. Even for slightly ionized substances a rigorous treatment involves the use of activity measurements or theory.

The ionization constant of acetic acid is formulated:

$$\frac{[H^+]\,[C_2H_3O_2^-]}{[HC_2H_3O_2]} = K \text{ (at const. temperature)},$$

the value for the constant may be derived by measuring electrical conductance since one may estimate limiting or maximum values for equivalent concentrations of all substances from measurements made at great dilutions. The limiting value of the conductance per gram equivalent of acetic acid is obtained indirectly by: Limiting equivalent conductance values for $HCl + NaC_2H_3O_2 - NaCl =$

limiting equivalent conductance value for $HC_2H_3O_2$. The measured value per gram equivalent of acetic acid at any concentration divided by the limiting value gives the fraction of 1 equivalent that is ionized. Using α as the symbol of the fraction ionized we then have $1 - \alpha$, of non-ionized acid, or $\frac{1 - \alpha}{V}$ is the molecular concentration of the non-ionized acid if V is the volume per gram molecule of acid originally used; $\frac{\alpha}{V}$ will be the concentration of either hydrogen ion or acetate ion, since the ionized fraction, α, is split into these two ions.

Hence $$\frac{\frac{\alpha}{V}\frac{\alpha}{V}}{\frac{1 - \alpha}{V}} = K, \quad \text{or} \quad \frac{\alpha^2}{(1 - \alpha)V} = K.$$

Proceeding in this fashion, Kendall[1] found values ranging from 1.81×10^{-5} to 1.85×10^{-5} at 25° C. for molalities ranging from 0.13 to 0.001. At higher concentrations there was a drift in the values for K. In the following table are given values rounded to four significant figures for the ionization constant of acetic acid.[2] The values under the column headed K' are derived from the conductance measurements without correction for activity effects, while those under K are corrected for activity effects.

THE IONIZATION CONSTANT OF ACETIC ACID AT 25° C.

Molar Concentration	$K' \times 10^5$	$K \times 10^5$
0.000114	1.779	1.754
0.001028	1.797	1.751
0.005912	1.823	1.749
0.01283	1.834	1.743
0.05000	1.849	1.721
0.1000	1.846	1.695
0.2000	1.821	1.645

It is evident that a good degree of constancy is attained over a two thousandfold concentration range. A limiting value of

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[1] J. Kendall, Medd. Vetenskapsakad. Nobel Inst., **2**, No. 38 (1911).

[2] Selected from a more extensive table established by D. A. MacInnes and T. Shedlovsky, J. Am. Chem. Soc. **54**, 1429 (1932).

$K = 1.753 \times 10^{-5}$ as derived by calculation from these measurements agrees well with the value 1.75×10^{-5} obtained independently from electromotive force measurements.[1]

Our present purposes will be served by using a rounded value of 1.75×10^{-5} for the constant. Some illustrations of the ways of utilizing such constants are given at the end of this Chapter and in Chapter VII.

When conductance measurements were applied in the same simple fashion to the estimation of constants for highly ionized substances like the majority of the common inorganic acids, bases and salts it was found that there was no approach toward constancy, even in dilute solutions, as is indicated by the data in Table IV.

TABLE IV. DISSOCIATION CONSTANTS CALCULATED FROM CONDUCTANCE MEASUREMENTS OF CERTAIN HIGHLY IONIZED SUBSTANCES.[2]

Molar Conc'n	KCl		HCl		KOH		$NaC_2H_3O_2$	
		K		K		K		K
0.001	0.973	0.043	(0.993)	(0.14)	(0.981)	(0.06)	(0.958)	(0.022)
0.01	0.941	0.16	0.972	0.34	0.917	0.10	0.894	0.077
0.1	0.861	0.56	0.920	1.06	0.894	0.75	0.778	0.273
1.0	0.755	2.3	0.791	3.0	0.771	2.6	0.525	0.58
3.0	0.679	4.3	0.565	7.2	0.590	2.6	0.278	0.32

This behavior was called *the anomaly of strong electrolytes.* The original assumptions were of course in error in disregarding the high concentrations of charged particles in solutions of these electrolytes and the effects of these charges upon each other and upon the dielectric properties of the solvent as the concentration of the electrolyte is changed. Some contrasts between the views advanced in the original theory of Arrhenius and those which have resulted from the researches of N. Bjerrum, A. A. Noyes and others regarding highly ionized electrolytes are here summarized:

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[1] H. S. Harned and B. B. Owen, J. Am. Chem. Soc., **52**, 5079 (1930).

[2] From L. Michaelis, Hydrogen Ion Concentration, transl. by W. A. Perlzweig, p. 112. Williams and Wilkins Co., 1926.

HIGHLY IONIZED ELECTROLYTES

Classical Ionic Theory	*Modern Views*
1. At any given concentration the active masses of the ions of a uni-univalent electrolyte, e.g., NaCl, are equal.	1. The activities of the anion and cation are in general unequal. At high dilutions the activities of the potassium and the chloride ion are assumed to be equal.
2. Incomplete ionization. The thermodynamic properties of the solution should not be additively those of the ions except at extreme dilutions.	2. Complete ionization. The thermodynamic properties of the solution are additively those of the ions to a marked degree even in concentrated solutions.
3. In a solution containing hydrochloric acid and potassium, sodium, or lithium chloride the per cent of the acid ionized should be less than that of an equivalent solution of the acid in water. This is the common ion effect, and it should be the same for equal concentrations of the salts.	3. Hydrochloric acid may have a greater activity in the presence of an alkali chloride than in pure water. In equivalent mixtures the activity of the acid is greatest in lithium chloride solution, less in sodium chloride solution and least with potassium chloride.
4. The active masses of the ions were thought to be independent of specific electrical forces, and not greatly affected by hydration.	4. The activity coefficient of an ion under given conditions depends upon its valence, dimensions, concentration in the solution and upon its electrical action upon other ions and upon the solvent molecules.

The classical ionic theory made possible a systematic treatment of the analytical chemistry of aqueous solutions, and it still serves to give a roughly quantitative treatment of those processes that involve ionic equilibria, namely precipitation, neutralization, complex-formation and oxidation-reduction reactions. The more concentrated the solutions and the higher the valences of the ions that are involved, the greater the errors that will be made in using molecular concentrations as active masses.

The non-ionized molecule as postulated in the classical theory is now believed not to exist in solution in many instances. Many salts are apparently made up of ionic lattices in the solid state. In the liquid state, or in suitable solvents of high dielectric constants the ions are free to move independently. In solution, simple electrolytes of this class, such as the alkali halides, are apparently completely ionized, but their ions are not independent of mutual electrical interaction except at extreme dilutions.

Many of the mineral acids, e.g., HCl, HBr, HI, HNO_3, $HClO_4$, etc., appear to be completely ionized in aqueous solution and active to the same extent in solutions of the same normality. The so-called "leveling" effect of water masks any intrinsic difference in the relative strengths of these acids. It is believed that essentially complete reactions of the type:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

occur in all of these cases. It is only in other solvents or at high concentrations in water that intrinsic differences in the acidic properties of these compounds are measurable. The proton, H^+, is to all intents and purposes completely solvated to form the oxonium (or hydronium) ion, H_3O^+. The ions of salts and bases are also solvated, presumably with a coordinated shell of water molecules of number depending upon the electronic structure of the ion. It is not necessary to attempt to write equations indicating the extent of solvation that exists as long as we are dealing with a single solvent, water. In many cases no exact data are available.

The following is an illustration of the use of an ionization constant: Given the ionization constant of benzoic acid = 6.86×10^{-5}, to find: (a) The hydrogen ion concentration; (b) The degree of ionization; and (c) The per cent of ionization, all in a 0.0500 molar solution of the acid.

(a) Calculation of the hydrogen ion concentration.

$$\frac{[H^+]\,[C_6H_5COO^-]}{[C_6H_5COOH]} = 6.86 \times 10^{-5} = 10^{-4.16}$$

If x equals the number of moles of hydrogen ion formed, that for benzoate ion will also be x, and the amount of undissociated acid in moles is $0.0500 - x$. Then

$$\frac{x \cdot x}{0.0500 - x} = 10^{-4.16} \text{ is solved for } x.$$

$$0.0500 = 5 \times 10^{-2} = 10^{-1.3}, \text{ and}$$

$$x^2 + 10^{-4.16}x - 10^{-5.46} = 0.$$

$$x = -\frac{10^{-4.16}}{2} \pm \sqrt{\frac{10^{-4.16^{2}}}{2} + 10^{-5.46}}$$

Only the positive root has physical significance.

$$x = 10^{-2.74} = 1.83 \times 10^{-3} \text{ moles/liter.}$$

In calculations of this type, if the x in the denominator is apt to be negligible, as in the present instance, relative to the quantity from which it is subtracted, the calculation may be greatly simplified:

$$\frac{x^2}{0.0500} = 10^{-4.16};\ x^2 = 10^{-5.46};\ x = 10^{-2.73},$$

or $x = 1.86 \times 10^{-3}$. It is recommended that in any calculation of this general nature the simpler approximate method as just used be tried. If the value found for x in this way is a small percentage, e.g., 1–5 per cent, of the value from which it would be subtracted in the denominator, the more exact type of calculation need not be used.

(b) *Calculation of* α, the degree of ionization. Having already found moles of hydrogen ion formed from 0.05 mole of the acid, the amount formed from 1 mole may be calculated by proportion:

$$0.0500 : 1.86 \times 10^{-3} = 1 : x$$

$$x = 0.0372.$$

Using the formula:

$$\frac{\alpha^2}{(1 - \alpha)V} = 10^{-4.16},$$

and using for V twenty, the number of liters containing 1 gram molecule, and neglecting α relative to 1 in the denominator,

$$\frac{\alpha^2}{20} = 10^{-4.16};\ \text{or } \alpha^2 = 10^{-2.86};\ = 10^{-1.43} = 0.0372$$

(c) *Per cent ionized.* Since α is part ionized per one part, per cent ionized which is parts ionized per 100 is simply obtained by proportion: $1 : \alpha = 100 :$ per cent. By definition the per cent ionized then equals 100 α, and in the present case 3.72 per cent of the acid is present in the form of its ions.

Activity. Debye and Hückel[1] have found a theoretical solution of the problem for calculating the individual activities of ions in very dilute solutions. The treatment is based upon

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[1] P. Debye and E. Hückel, Physik. Z. **24**, 185, 305 (1923).

electrical interaction between ions, their closeness of approach, and the dielectric properties of the solvent. Their limiting formula for dilute solutions makes it necessary to know only the ionic strength, μ, of the solution and the charges of the ions. Ionic strength as defined by G. N. Lewis is found by multiplying the molality of each ion by the square of its valence and dividing the sum of these terms by two.[1] The expression for the activity coefficient from the Debye-Hückel theory is:

$$\log f_i = -0.505\, Z_i^2 \sqrt{\mu}$$

where f_i is the activity coefficient of an ion of charge Z_i, μ is the ionic strength and the numerical term 0.505 is from terms involving dielectric constant and closeness of approach of the ions. If it is desired to calculate the mean activity coefficient for the ions of the salt, the expression is at 25° C.

$$\log f = -0.505\, Z_+ Z_- \sqrt{\mu}$$

Z_+ being the charge of the positive ion and Z_- that of the negative ion. Neither of these limiting formulae is applicable to solutions of very high ionic strength, but they apply well in the range from $\mu = 0.01$ and lower.

The way in which the Debye-Hückel limiting formula reproduces the values in dilute solution may be illustrated by calculating the value for barium chloride or any other salt of a bivalent ion and two univalent ones. For a 0.001 *M* solution the ionic strength,

$$\mu = \frac{2^2 \times 0.001 + 1^2 \times 2 \times 0.001}{2} = 0.003.$$

Hence $\log f = -0.505 \times 2 \times 1 \times \sqrt{0.003} = -0.0555$, and the activity coefficient, $f = 0.880$. See Table V, p. 86.

Experimentally it is possible only to determine the activity for *compounds*, i.e., values for non-ionized molecules, or mean activities for completely ionized substances. The activities of the ions or chlorides are derived from those of the compounds on the basis of assumptions of the following sort: (1) That in dilute potassium chloride solutions the activity of the chloride ion equals that of the potassium ion; (2) That in dilute solutions the

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[1] For mixtures of salts or double salts the sum of the calculated values for the ionic strengths of the separate salts is used.

activities of the chloride ion in solutions of the same normality are equal.

The measured activity coefficients in the following table will give an idea of the extent to which the active masses of various substances differ from the molecular concentrations at various dilutions.

TABLE V. ACTIVITY COEFFICIENTS OF VARIOUS SUBSTANCES.[1]

Concentration (M)	0.001	0.01	0.1	1.0	2.0
HCl	0.966	0.904	0.796	0.809	1.01
$HClO_4$	.....	.....	.....	0.81	1.04
HNO_3	0.965	0.902	0.785	0.720	0.783
NaOH	.....	.....	.....	0.68	0.70
KOH	.....	0.90	0.80	0.76	0.89
LiCl	0.963	0.89	0.78	0.76	0.91
NaCl	0.966	0.904	0.780	0.66	0.67
KCl	0.965	0.901	0.769	0.606	0.576
NH_4Cl	0.961	0.88	0.74	0.57	.....
H_2SO_4	0.830	0.544	0.265	0.130	0.124
$Ba(OH)_2$	.....	0.712	0.443	.....	.....
$BaCl_2$	0.88	0.72	0.49	0.39	0.44 (at 1.8M)
$Ba(NO_3)_2$	0.88	0.71	0.43	.....	.....
$CaCl_2$	0.89	0.725	0.515	0.71	.....
$Mg(NO_3)_2$	0.88	0.71	0.51	0.50	0.69
$CdSO_4$	0.73	0.40	0.17	0.045	0.033
$ZnSO_4$	0.70	0.39	0.15	0.045	0.036
$Al(NO_3)_3$	.....	.....	0.20	0.19	0.45
$K_4Fe(CN)_6$	.....	.....	0.14	.....	.....

The activity coefficients in general pass through a minimum and then rise steadily, frequently exceeding the value 1 in the range 1–3 *M*.

MODERN VIEWS REGARDING ACIDS AND BASES

It is stated in Chapter VII, p. 111, that the equilibrium in a neutralization depends upon the competition of the various substances for hydrogen ion, symbolized there as H^+, for purposes of simplicity. More strictly speaking, the hydrogen ion in aqueous solution is H_3O^+, which results from the combination of the proton, H^+, with the solvent. As the behavior of acids

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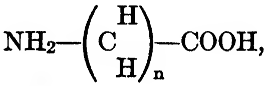
[1] From a collection given by W. M. Latimer, Oxidation Potentials, Prentice-Hall, Inc., New York. Copyright 1938. Reproduced with permission.

in various solvents is considered it becomes evident that the vital or central point about neutralizations is the equilibrium between protons and any substance with which they unite.[1] The new general definition of an acid is "a substance having the chemical property of losing a proton to another substance."[2] A base is formed in the process: Acid $\rightleftharpoons$ Proton + Base. Conversely, a base is a substance that combines with protons to form an acid. Acids may be either neutral molecules or positive or negative ions:

$$\begin{array}{rcll}
\text{Acid} & & \text{Proton} & \quad \text{Base} \\
HCl & \rightleftharpoons & H^+ & + \; Cl^- \\
H_2PO_4^- & \rightleftharpoons & H^+ & + \; HPO_4^- \\
NH_4^+ & \rightleftharpoons & H^+ & + \; NH_3 \\
Fe(H_2O)_6^{+++} & \rightleftharpoons & H^+ & + \; Fe(H_2O)_5OH^{++} \\
H_3O^+ & \rightleftharpoons & H^+ & + \; H_2O \\
H_2O & \rightleftharpoons & H^+ & + \; OH^-
\end{array}$$

The base may also be either a positive or negative ion or a neutral molecule. Water has both acidic and basic properties, as have many other substances, e.g., amino acids



$$NH_2-\left(\begin{array}{c}H\\C\\H\end{array}\right)_n-COOH,$$

ions like HCO_3^-, $HPO_4^=$, etc.

From the modern point of view there is thus a duality in acid-base systems in which each acid has related to it a conjugate base. If a base belonging to another conjugate acid-base system

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[1] The modern view has been developed primarily by Bronsted, and by Lowry. J. N. Bronsted, Rec. Trav. Chim. **42**, 718 (1923); Chem. Reviews **5**, 231 (1928); on pp. 284–312 the view is presented in detail. T. M. Lowry, Chem. & Ind. **42**, 43 (1923); Trans. Faraday Soc. **20**, No. 13 (1924). Some further reviews of the subject are given by: N. F. Hall, J. Chem. Education **7**, 782 (1930); M. Kilpatrick, *ibid.*, **12**, 109 (1935); J. P. McReynolds, J. Chem. Education **17**, 116 (1940); N. F. Hall, *ibid.*, **17**, 124 (1940); H. T. Briscoe, *ibid.*, **17**, 128 (1940); L. P. Hammet, *ibid.*, **17**, 131 (1940); W. C. Johnson, *ibid.*, **17**, 132 (1940).

[2] H. N. Alyea, et al. (Report of the Committee on Nomenclature of Acids and Bases, J. Chem. Ed. **16**, 535 (1939).

is added, the two bases compete for association with the protons. Example: Hydrogen chloride when added to water reacts as follows:

$$\underset{\text{acid}_1}{HCl} + \underset{\text{base}_2}{H_2O} = \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{Cl^-}$$

The reaction in this case runs to the disappearance of the HCl molecules. With acetic acid the equilibrium is reached after a very small percentage of the acid has reacted. In the hydrolysis of ammonium chloride the equilibrium depends upon the competition between the bases NH_3 and water for the proton of the ammonium ion:

$$\underset{\text{acid}_1}{NH_4^+} + \underset{\text{base}_2}{H_2O} \rightleftharpoons \underset{\text{acid}_2}{H_3O^+} + \underset{\text{base}_1}{NH_3}$$

The modern view is useful in understanding the neutralizations that occur in solvents other than water. For example, a solution of ammonium nitrate dissolved in liquid ammonia has acidic properties. It will dissolve magnesium, sodium, etc., to give hydrogen; if potassium amide is added a titration may be performed with the aid of an indicator or electrometrically. The ammonium ion is an acid in liquid ammonia, and the amide ion NH_2^- is a far stronger base than is ammonia, NH_3, which is here the neutral solvent. Hence in liquid ammonia the reaction $NH_4^+ + NH_2^- = 2NH_3$ proceeds virtually to completion. In anhydrous acetic acid[1] acids such as hydrochloric, perchloric, etc., are strongly acid (superacid) relative to the anhydrous acetic acid, and they may be used to titrate many basic substances in this solvent, as for example sodium acetate, organic amines, etc. In this solvent acetate ion is a strong base and combines readily with the proton derived from any sufficiently strong acid., e.g., perchloric, the strongest, sulfuric acid next and hydrochloric third. The relative strengths of the three acids are found to be appreciably different in anhydrous acetic acid, although all are satisfactory for the titration of many bases in this medium.

Neutralizations in various alcoholic solvents are frequently used for the determination of many organic acids which are only

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[1] N. F. Hall and J. B. Conant, J. Am. Chem. Soc. **49**, 3047 (1927); Conant and Hall, *ibid.*, **49**, 3062 (1927); N. F. Hall and T. H. Werner, *ibid.*, **50**, 2367 (1928).

slightly soluble in water. The hydroxyl ion and the ethylate ion, $OC_2H_5^-$, are strong bases in these solvents. Sodium or potassium hydroxide or sodium ethylate is a convenient form in which to introduce these ions. It is a noteworthy fact that the relative strengths of two acids or bases may be shifted as we use a solvent other than water. A case in point for an alcoholic solution is that the ratio of the ionization constant of picric acid to that of benzoic acid is shifted very considerably in N-butanol from its value in water.[1]

Finally it should be mentioned that much of the pioneer work upon the general relationships of acid-base systems other than water was done by the late E. C. Franklin and his associates. In summaries of this work much stress is laid upon the fact that bases may be derived by replacing one hydrogen atom of the molecule of the solvent by a metallic ion; for example that KOH, KNH_2, KSH, KHF_2, etc., are the characteristic bases of the water, ammonia, hydrogen sulfide and hydrogen fluoride systems respectively.[2] The more recent view, as has been pointed out here, emphasizes the nature of the acid function, and the duality of acid-base relationships.

REVIEW QUESTIONS AND PROBLEMS

1. Taking the atomic weight of oxygen as 16.000; light hydrogen as 1.000 and that of deuterium as 2.000, and of the carbon isotopes as 12.000 and 13.000 respectively, calculate the respective weights of water and of carbon dioxide obtained upon burning 0.2000 g. (a) Of $C^{12}H_4$; (b) Of $C^{13}H_4$; and (c) Of $C^{13}D_4$.

Ans. (a) CO_2 0.5500 (b) 0.5294 (c) 0.4286
H_2O 0.4500 0.4235 D_2O 0.3809

2. In 1920 the law of definite proportions was commonly stated: "Every chemical compound consists of the same elements combined in the same proportions by weight, wherever it occurs." Comment upon this definition in the light of the present state of our knowledge.

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[1] According to data of Wooten and Hammet the ratio is shifted 100-fold, J. Am. Chem. Soc. **57**, 2289 (1935); see also Mason and Kilpatrick, *ibid.*, **59**, 572 (1937). Evans and Davenport proved experimentally that this shift may be used to develop a method of estimating the two acids when both are present in a mixture, *ibid.*, **59**, 1920 (1937).

[2] A broad summary of these views is given by E. C. Franklin, J. Am. Chem. Soc. **46**, 2137 (1924).

3. Formulate equilibrium expressions for: (a) The ionization of phosphoric acid (first step). (b) The ionization of ammonium hydroxide. (c) The oxidation of stannous ion by ferric ion.

4. Given the ionization constant of hydrocyanic acid $= 7 \times 10^{-10}$, calculate the degree of dissociation, the per cent of ionization and the hydrogen-ion concentration in a 1.000 molar solution of the acid. (Neglect α relative to 1, in the term $1 - \alpha$.)

5. Make the same computations as in problem 4, for boric acid regarded as HBO_2, of ionization constant 6.6×10^{-10}, in a 0.500 molar solution.

6. What is the ionic strength of a 0.0002 molar solution of aluminum chloride? Calculate the mean activity coefficient for aluminum chloride at this concentration. Ans. $\mu = 0.0012$; $f = 0.885$. (This value is hypothetical because hydrolysis occurs.)

7. Calculate the ionic strength and the activity coefficient of calcium chloride in 0.01 molar solution. Ans. $\mu = 0.03$; $f = 0.67$.

8. Write the ionization constant of acetic acid in terms of activity coefficients and molecular concentrations. If each activity coefficient is 0.9, calculate the hydrogen-ion concentration in a 0.1000 molar solution, using the approximation formula. Make the same calculation assuming the activity coefficients to be unity in all cases. Take 1.8×10^{-5} as the ionization constant. Ans. (a) 1.4×10^{-3}; (b) 1.34×10^{-3}.

CHAPTER VI

THE GENERAL PRINCIPLES OF VOLUMETRIC ANALYSIS

CALIBRATION OF APPARATUS

Volumetric analysis consists in determining the volume of a solution of known concentration which is needed to react quantitatively with a solution of a weighed or volumetrically measured quantity of material. The weight of active material is calculated from the volume of reagent used.[1]

The process of measuring the volume of solution that is needed to complete the reaction is called *titration.* The point at which some detectable evidence indicates the completion of the reaction is called the *end-point.* The end-point should coincide as closely as possible with the point at which chemically equivalent amounts of the reagent and the substance titrated have been brought into reaction. This latter point is called the *equivalence-point,* or *stoichiometric point.* Whenever the visible end-point does not coincide exactly with the equivalence-point, it is desirable to determine the strength of the reagent and to perform the analyses under precisely similar conditions.

A reaction must fulfill the following conditions to be suitable for use in volumetric analysis: 1. It must go practically to completion when equivalent amounts of the reacting substances are present; 2. It must be practically instantaneous; 3. The end-point must be sharply defined by some change in the physical or chemical properties of the solution, such as a change in color, or the formation of a precipitate. When the reagents themselves do not make this possible, a third substance is added, known as an *indicator,* which reacts only when the main reaction is completed.

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[1] In very precise investigations the weight of solution may be determined, using a weight buret. An excellent type of weight buret has been described by Friedman and La Mer, Ind. Eng. Chem. Anal. Ed. **2**, 54 (1930). See p. 103.

If a reaction is not quite rapid enough, or if it must be accelerated to completion by a small excess of reagent, it may still be used in some instances by combining it with a reaction which satisfies the requirements of the experiment, and using the latter reaction to titrate the excess of the reagent.

The number of reactions suitable for volumetric analysis is comparatively small, and many reactions which are otherwise satisfactory cannot be used because there is no indicator which will show when the end-point is reached. For example, the process of dissolving ferric oxide in hydrochloric acid to form ferric chloride fulfills none of the volumetric requirements. The solution of calcium carbonate in acid requires more than the theoretical amount of acid, and even then, the reaction is not instantaneous; by titrating the excess of the acid remaining, it is possible to determine the amount required to unite with the carbonate.

Volumetric methods are often more accurate than gravimetric methods, especially when the latter are subject to errors which are not easily avoided. For this reason, iron, chromium, arsenic and antimony are best determined volumetrically. Tedious and difficult separations are often thus avoided, and the process becomes more rapid than a gravimetric method. In many cases, however, gravimetric methods show greater precision.

TYPES OF REACTIONS IN VOLUMETRIC ANALYSIS

The reactions used in volumetric analysis fall into two broad classes: (a) Those which do not involve changes in valence, and (b) Oxidation-reduction reactions. For purposes of convenience, however, these reactions may be divided into three classes: [1]

1. **Acidimetry and Alkalimetry, or Neutralization Reactions** involve only the neutralization of acids and bases, either present as such or formed from acid or basic salts or by hydrolysis. These reactions involve the union of hydrogen and hydroxyl ions to form water. The standard solutions are strong acids or bases

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[1] For a discussion of typical volumetric methods of organic chemistry, as, for example, esterification, halogen addition, substitution, etc., see I. M. Kolthoff, Volumetric Analysis, Vol. I (translated by N. H. Furman). J. Wiley & Sons, Inc., New York.

(hydroxides), and sometimes salts which react acid or alkaline due to hydrolysis.

2. **Precipitation and Complex-formation Reactions** involve only the interchange of ions and may be divided into two classes: those in which simple precipitation occurs, as in the titration of silver with the solution of a chloride, and those in which a complex ion is formed, as in the titration of the cyanide ion with silver nitrate, in which the ion $Ag(CN)_2^-$ is formed. No change in valence occurs, nor are hydrogen and hydroxyl ions involved.

3. **Oxidation-Reduction Reactions** involve changes in oxidation number (p. 192) or state of oxidation of the reacting substances. The standard solutions are either oxidizing or reducing agents.

In order to perform volumetric analyses it is necessary to have: (a) Solutions of known concentration, and hence substances of known purity. (b) Some means of detecting the completion of the reaction, i.e., some sort of indicator. Indicators for the various types of reactions are discussed in Chapters VII, IX and X. (c) Calibrated apparatus, including burets, pipets and flasks.

STANDARD SOLUTIONS

Solutions of known concentration, called *standard solutions,* may be prepared either empirically or on the basis of theoretical considerations.

An *empirical standard solution* is prepared in such a manner that 1 ml. of it reacts with some definite, convenient quantity of another substance, as for example with 5 mg. This is often desirable when the solution is to be used in the determination of only one substance, but different empirical solutions bear no simple relation to each other.

A *molar solution* contains one gram molecular weight of solute per liter of solution. In volumetric analysis, solutions are generally prepared on the normal basis.

A *normal solution* (*N*) contains one gram equivalent weight of the solute per liter of solution. Any convenient multiple or fraction of the equivalent weight may be used when a normal solution is too weak or too strong for the purpose at hand. Solutions containing one-half, one-tenth, and one-twentieth of a gram equivalent per liter are most frequently used; they are designated as 0.5, 0.1, and 0.05 *N* respectively, or sometimes as *N*/2, *N*/10, and *N*/20. Equal volumes of all normal solutions are therefore equivalent to each other when used for the same type of reaction. Since the above definition utilizes the terms "equivalent," "equivalent weight" or "hydrogen equivalent" (which are synonyms), it becomes necessary to define these terms. No definition will cover completely all types of reactions, and as this subject is difficult for the student, it will be discussed in considerable detail in the following paragraphs.

The Equivalent Weight or Hydrogen Equivalent of a Substance. Acidimetry and Alkalimetry. In this type of reaction, the equivalent of a reagent is the amount of the reagent which contains or reacts with one gram atom of replaceable hydrogen or with one gram molecule of hydroxyl. For example, barium hydroxide, $Ba(OH)_2$, contains two hydroxyl groups; therefore the equivalent is one-half of the molecular weight or $\frac{Ba(OH)_2}{2}$. Sodium carbonate, Na_2CO_3, reacts with two gram atoms of hydrogen in hydrochloric acid to form two gram molecules of sodium chloride; therefore its equivalent weight is $\frac{Na_2CO_3}{2}$.

Precipitation and Complex-formation Reactions. In this type of reaction, the equivalent is the amount of the substance which contains or reacts with one gram atom of a univalent cation, one-half gram atom of bivalent cation, etc. In the case of the cation the equivalent is, therefore, the atomic weight divided by the valence; in the case of a reagent which reacts with this cation, the equivalent is the amount which reacts with one equivalent of the cation. Thus it will be seen that the cation or metal is taken as the standard. Alkali metals, however, are almost never considered. For example, the equivalent weight of silver nitrate, $AgNO_3$, is its molecular weight because silver has a valence of one; since two molecules of potassium cyanide react with one atom of silver, the equivalent weight of the cyanide is 2KCN. The equivalent weight of nickel is $\frac{Ni}{2}$. If it requires four molecules of potassium cyanide to react with one atom of nickel, forming $K_2Ni(CN)_4$, then it would require 2KCN to react with $\frac{\text{Ni}}{2}$, and the equivalent weight of the reagent would again be 2KCN. In these cases, the alkali metal has nothing to do with the equivalent. In determining which metal is to be taken as standard, one should consider whether the anion or cation is involved in the reaction, and whether some other metal could be substituted without essentially changing the reaction. This will be clear if the reaction is written as an ionic equation. Thus, in the instance just mentioned, the cyanide ion and not the sodium or potassium ion is involved in the reaction; therefore the potassium ion is not considered in determining the equivalent.

Oxidation and Reduction Processes. In this type of reaction, the equivalent weight is the amount of a reagent which contains or reacts with one gram atom of available hydrogen, one-half gram atom of available oxygen, or an equivalent amount of some other element such as chlorine, bromine, or iodine. "Available" means capable of being used in the oxidation or reduction. Since the oxidation and reduction of metals involve a change in their valence, the equivalent in such cases may be defined as the molecular weight divided by the change in valence. If, instead of valence, the "oxidation number" is considered,[1] the definition given above may be extended to include all elements by the statement that the equivalent of any substance is its molecular weight divided by the change in oxidation number of the amount of the particular element involved which occurs in the molecular formula of the substance. The student must be thoroughly familiar with the method of finding and using this "oxidation number," not only because of the reasons just stated, but also because it helps in the balancing of equations involving oxidation and reduction. It should be noted that any reaction in which there is a change in the oxidation number of the element to be determined comes in this class. If there is no change, the reaction does not belong here. For example, if potassium permanganate, $KMnO_4$ is reduced to manganous sulfate, $MnSO_4$, the oxidation number of manganese changes from +7 to +2; hence the equivalent is $\frac{KMnO_4}{5}$. If oxalic acid, $H_2C_2O_4$, is

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[1] See McAlpine and Soule, Qualitative Chemical Analysis, D. Van Nostrand Co., 1933, pp. 637 and ff.

oxidized to water and carbon dioxide, one atom of oxygen or two equivalents are required, and the hydrogen equivalent is $\frac{H_2C_2O_4}{2}$. Or, the oxidation number of the carbon in one molecule (C_2) changes from + 6 to + 8, which gives the same result.

This discussion is proof that in volumetric analysis the equivalent of a substance is not a fixed quantity, but is dependent upon the reaction in which it is used. The same substance may have several different equivalents. Thus chromic acid, H_2CrO_4, as an acid has an equivalent of $\frac{H_2CrO_4}{2}$ since it contains two replaceable hydrogen atoms, but when used as an oxidizing agent ($Cr^{VI} \rightarrow Cr^{III}$; or $CrO_4^{=} + 8H^{+} + 3e \rightarrow Cr^{+++} + 4H_2O$) it contains three equivalents per molecule, and its equivalent is $\frac{H_2CrO_4}{3}$. As an acid, the equivalent of iodic acid, HIO_3, is the molecular weight; as an oxidizing agent, when reduced to hydrogen iodide, HI, its equivalent is $\frac{HIO_3}{6}$. Potassium permanganate, $KMnO_4$, may be reduced to a manganous salt, giving an equivalent of $\frac{KMnO_4}{5}$; to manganese dioxide, MnO_2, giving an equivalent of $\frac{KMnO_4}{3}$; to trivalent manganese, giving an equivalent of $\frac{KMnO_4}{4}$; or to the manganate, K_2MnO_4, giving an equivalent of $\frac{KMnO_4}{1}$.

In determining the equivalent of a substance in volumetric analysis it is, therefore, essential to give the reaction involved. The entire equation need not always be written, but the changes undergone by the substance must be known. Thus, to determine the equivalent of potassium bichromate, $K_2Cr_2O_7$, as an oxidizing agent one must know that it is reduced to a chromic salt (Cr^{+++}). It makes no difference how this reduction is accomplished or what reducing agent is used for the purpose. The oxidation number of the chromium (Cr_2) in one molecule of the bichromate changes from + 12 to + 6, so that the equivalent is $\frac{K_2Cr_2O_7}{6}$. This oxygen is, of course, never given off in the free form, but is taken up by the reducing agent.* One should remember that in volumetric analysis there is no definite equivalent without a reaction. When the equivalent of a compound is known, that of any part of it is easily obtained. Thus if the equivalent of potassium bichromate is $\frac{K_2Cr_2O_7}{6}$, that of chromic oxide is $\frac{Cr_2O_3}{6}$ and that of chromium $\frac{Cr_2}{6}$ or $\frac{Cr}{3}$. If the equivalent of iron is the atomic weight, then that of ferric oxide must be $\frac{Fe_2O_3}{2}$ since $\frac{Fe_2}{2} = Fe$. One reaction, e.g., oxidation of ferrous to ferric ion ($Fe^{++} \rightarrow Fe^{+++}$), may thus serve to determine the equivalent of iron and its compounds, Fe, FeO, Fe_2O_3, Fe_3O_4, $FeSO_4$, etc., when used in oxidation-reduction processes.

When several reactions are involved in a process, *the reaction which determines the equivalent is the one in which the standard solution is used. The equivalent of a substance is always that amount which reacts with, is formed by, or, in general, corresponds to the equivalent of the active reagent in the standard solution.* This statement is of very great importance. Thus, if potassium nitrate is reduced to ammonia and the latter titrated with standard acid, the equivalent of potassium nitrate is not determined by the reduction but by the reaction between ammonia and acid. Since the equivalent of ammonia is $\frac{NH_3}{1}$, that of the nitrate is $\frac{KNO_3}{1}$, since one molecule of the nitrate yields one of ammonia.

The following exercises will be found useful to give practice in finding equivalents. In each of them proceed as follows: 1. Write the actual, or if it is an oxidation-reduction reaction, the hypothetical equation. 2. Name the class of volumetric reactions to which it belongs. 3. Indicate the change in oxidation number, if any occurs. 4. Give the equivalent of the first sub-

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* Even when no oxygen is involved, it is always possible to devise an equation which will be expressed in terms of oxygen. Thus, the equation $SnCl_2 + Cl_2 = SnCl_4$ may be written $SnCl_2 + O + 2HCl = SnCl_4 + H_2O$, showing that the equivalent of stannous chloride is $\frac{SnCl_2}{2}$. Such hypothetical equations may be very useful in the determination of equivalents.

stance in each case with reasons for your choice. Do not calculate the molecular weight.

1. H_2CrO_4 to Na_2CrO_4
2. H_2CrO_4 to $CrCl_3$
3. HIO_3 to HI
4. N_2H_4 to N_2
5. H_2SO_3 to H_2SO_4
6. $FeCl_2$ to $K_4Fe(CN)_6$
7. KCN + $NiCl_2$ to $K_2Ni(CN)_4$
8. CuCNS to HCN and $CuSO_4$
9. KI + $HgCl_2$ to K_2HgI_4
10. $Na_2B_4O_7$ to NaCl and H_3BO_3
11. AsH_3 to H_3AsO_4
12. $Na_2S_4O_6$ to Na_2SO_4
13. PCl_5 to 5NaCl + Na_2HPO_4
14. Na_2SiF_6 to ThF_4 and H_4SiO_4
15. HNO_3 to NH_3
16. $KMnO_4$ to K_2MnF_5
17. $HgCl_2$ to Hg
18. KF to K_3FeF_6
19. $K_2S_2O_8$ to K_2SO_4
20. $K_2S_2O_7$ to K_2SO_4
21. $NaClO_2$ to NaCl
22. Na_3PO_4 to NaH_2PO_4
23. KNO_2 to NO

Preparation of Standard Solutions. There are two general methods of preparing such solutions: 1. *Direct Method.* This method consists in dissolving the equivalent weight, or a definite fraction or multiple thereof, of a substance of known purity in the solvent, usually water, and making uniform after dilution to the proper final volume. 2. *Indirect Method.* A solution of approximately the desired normality is prepared, and then standardized by titrating with it the solution of a substance of known purity (cf. primary standard substances, p. 99).

It is not always possible to use the first or direct method. For example, an alkali such as sodium or potassium hydroxide cannot be obtained in a chemically pure condition. On the other hand, hydrochloric acid and water yield a constant-boiling mixture which has a definite composition and specific gravity if prepared at a known barometric pressure. The appropriate weight of such acid may be diluted to a liter and mixed thoroughly to make a solution of any desired normality, e.g., 1.0, 0.5, or 0.1 *N*.

The following are some important substances which may be obtained rather easily in a condition of suitable purity for the direct preparation of standard solutions, and are therefore primary standards: benzoic acid, potassium acid phthalate, sodium carbonate, potassium chloride, sodium chloride, silver or silver nitrate, potassium bromate, potassium iodate, potassium bichromate, arsenious oxide, iodine, and sodium oxalate.

Solutions of most acids other than hydrochloric acid, of the alkalis, and of the very useful reagents potassium permanganate and sodium thiosulfate, are generally prepared by the indirect method.

The indirect method requires standardizations to establish the normalities of the solutions. The process of standardization is carried out exactly as an analysis, except that in this case the weight of the active substance that is titrated is known, and the normality of the reagent is unknown. Both the direct and indirect methods therefore require substances of known and preferably of complete purity, that is, primary standard substances.

Primary standard substances should have the following characteristics in order to be ideally satisfactory:[1] 1. Easy to obtain, purify, and dry, preferably at 100–105° C., without change in composition. This requirement is not met by substances which have water of crystallization. 2. Capable of being tested for impurities by simple and delicate qualitative tests of known sensitivity. 3. Unalterable in air during weighing, and, if possible, stable in contact with air of average humidity over long periods, i.e., not hygroscopic, not oxidized by air, not altered by carbon dioxide. 4. A high equivalent weight in order that weighing errors may have a small relative effect. 5. Reaction with the standard solution according to a single, well-defined, rapid, and essentially complete chemical process.

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[1] S. P. L. Sörensen, Z. analyt. Chem. **44**, 141 (1905); J. Wagner, Verh. d. Vers. Deutsch. Ntf. u. Ärzte, Abt. f. angew. Chem., II, p. 183 (1901); I. M. Kolthoff, Volumetric Analysis (Translated by N. H. Furman), published by J. Wiley & Sons, Inc., New York, Vol. I, p. 248, Vol. II, pp. 38–48.

In practice, a compromise between these several ideal requirements is generally necessary. The substances commonly used as standards are: Acidimetry and Alkalimetry—sodium carbonate, thallous carbonate, Tl_2CO_3,[1] succinic acid, $H_2C_4H_4O_4$, sulfamic acid, HSO_3NH_2,[2] potassium acid phthalate, $KHC_8H_4O_4$, benzoic acid, $HC_7H_5O_2$, constant boiling hydrochloric acid, and sometimes oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, although the latter can not be easily dried. Oxidizing agents—potassium bichromate, $K_2Cr_2O_7$, potassium bromate, $KBrO_3$, potassium iodate, KIO_3, iodine. Reducing agents—sodium oxalate, $Na_2C_2O_4$, arsenious oxide, As_2O_3, electrolytic iron. Precipitation or complex-formation—silver, silver nitrate, various metals and salts, depending on the particular reaction used.

It is theoretically possible to have a single standard substance which would serve in several or all of the branches of volumetric analysis. Potassium iodate, for example, may be used in the standardization of acids, or of reducing agents:

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O.$$

In this equation, the amount of iodine that is formed is chemically equivalent to the amount of that one of the three reactants which is not present in excess. Potassium iodate may be converted quantitatively into potassium iodide, and the latter used as a primary standard in precipitations or complex-formations. Sodium oxalate is used as a primary standard for permanganate solutions. The oxalate may also be converted into the carbonate by heat:

$$Na_2C_2O_4 = Na_2CO_3 + CO$$

and the carbonate used as a primary standard for acids. Most of the primary standards that have been investigated serve best in a single type of reaction.

It is generally preferable to standardize a solution by a reaction of the same type as that for which the solution is to be used, and as nearly as possible under identical conditions of total volume, concentration of acids, salts, and indicator. In

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[1] E. Jensen and B. Nilsen, Ind. Eng. Chem. Anal. Ed. **11**, 508 (1939).

[2] M. J. Butler, G. F. Smith and L. F. Audrieth, Ind. Eng. Chem. Anal. Ed. **10**, 690 (1938).

this way, errors due to the amount of reagent needed to react with the indicator, and to other factors, cancel out to a considerable extent.

THE MEASUREMENT OF SOLUTIONS. ERRORS

The precision of volumetric work depends upon the accuracy with which volumes of solutions can be measured. This is much less than the accuracy of weighing. There are certain sources

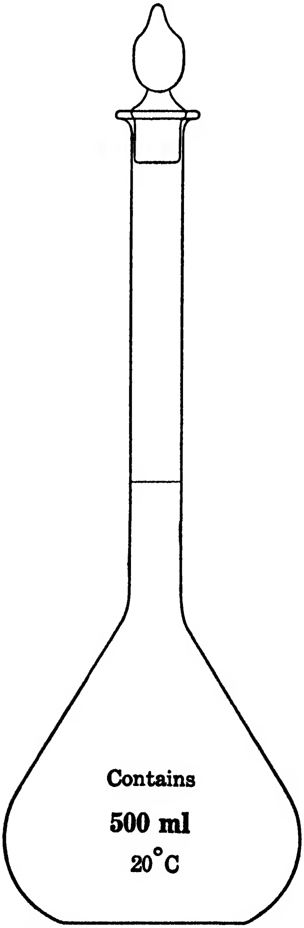

Fig. 26. Volumetric Flask.

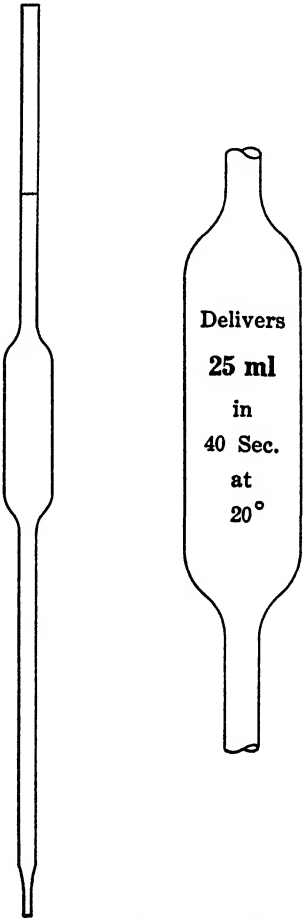

Fig. 27. Volumetric Pipet.

of error which must be carefully considered. Changes in temperature cause changes in the volume of glass apparatus and of solutions. An ordinary glass flask of 1000 ml. volume increases 0.025 ml. per degree, but if made of pyrex glass the increase is much less. 1000 ml. of water or of most 0.1 *N* solutions increases 0.20 ml. per rise of 1° C. at room temperature. There may be errors of calibration of the apparatus, that is, the volume marked on the apparatus may not be the true volume. Such errors can be eliminated only by recalibrating the apparatus. Another error common to all volumetric reactions is that involved in determining the end-point.

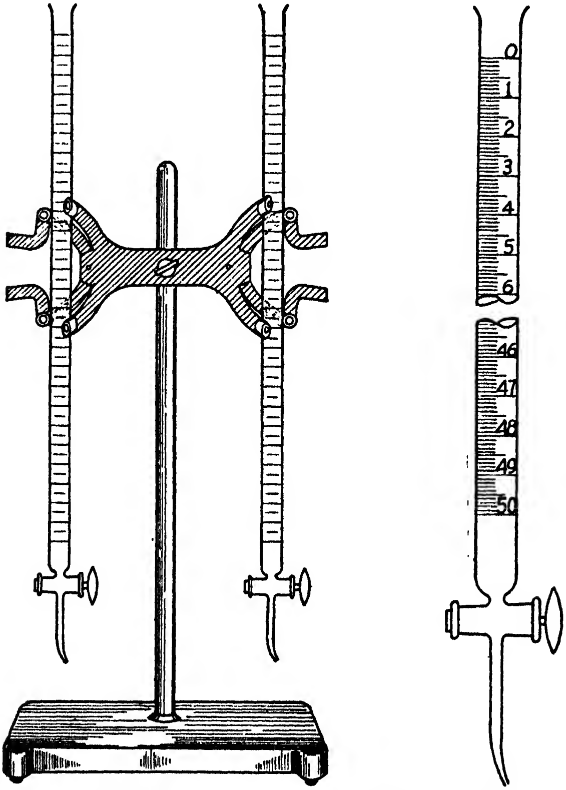

FIG. 28. A Buret. Fisher Holder with Burets.

Volumetric apparatus may be calibrated to contain or to deliver a definite volume of liquid. Flasks (see Fig. 26) are usually calibrated to *contain a given volume* when filled so that the bottom of the meniscus is tangent to the ring which has been etched on the neck of the flask, the eye being at the level of the ring.

Pipets (see Fig. 27) are calibrated to *deliver a fixed volume;* the usual capacities are 5, 10, 25, and 50 ml. They are used in the following way: The liquid is sucked up above the mark on the stem above the bulb, and the upper end is quickly closed with the dry index finger; any adhering liquid is wiped from the outside of the lower stem; the level is allowed to fall slowly by regulating the pressure on the finger, until the bottom of the meniscus is tangent to the mark. Liquid clinging to the tip is removed, and the pipet is allowed to empty freely into the receiving vessel; the tip of the pipet is kept in contact with the wall of the receiving vessel for a second or two after the free flow has stopped. *The liquid remaining in the tip is not removed;* this is most important.

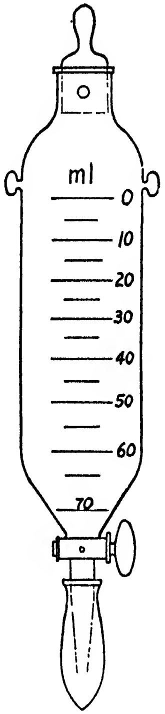

FIG. 29. A Weight Buret.

Burets (see Fig. 28) (a weight buret is shown in Fig. 29) are used to *deliver variable volumes.* They are usually of 50 ml. capacity graduated to tenths of a ml., and are provided with stop-cocks. The latter must be properly lubricated to avoid sticking or "freezing" and to prevent leakage.[1] See Fig. 30. The stopper should be held by a rubber washer or other suitable device. A 50 ml. buret must not be emptied faster than 0.7 ml. per second. Otherwise too much liquid will adhere to the walls and the volumes delivered will be too small. A reading would not remain constant, but as the solution drained down the meniscus would gradually rise.

A few general rules in regard to the manipulation of a buret may be of value. Do not try to dry a buret which has been

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[1] Suitable stop-cock grease may be purchased. Directions for its preparation are given by Bradley and Wilson, Ind. Eng. Chem. **18**, 1279 (1926); Shepherd and Ledig, *ibid.*, **19**, 1059 (1927).

cleaned for use, but rinse it out two or three times with a little of the solution with which it is to be filled. Do not allow alkaline solutions to stand in a buret, because the glass will be attacked and the stop-cock will tend to stick badly. The best method of reading a buret is to hold back of it, close to the glass, a card, the upper half of which is white and the lower black, with the dividing line just below the bottom of the meniscus. See Fig. 31. The top of the level of the liquid is read if the liquid is dark colored. Parallax may be eliminated by having the etched graduations run at least half way around the buret. If the upper part of the card is bent back at the dividing line at a slight angle it will act as a reflector and give better illumination. A buret with a blue line running down the back should not be used. Such burets are not as accurately read unless special means are taken to avoid parallax.

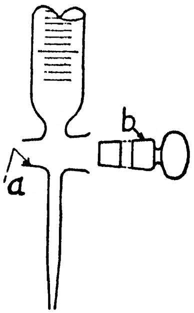

FIG. 30. Method of Greasing a Buret. The grease is applied lightly at points *a* and *b*.

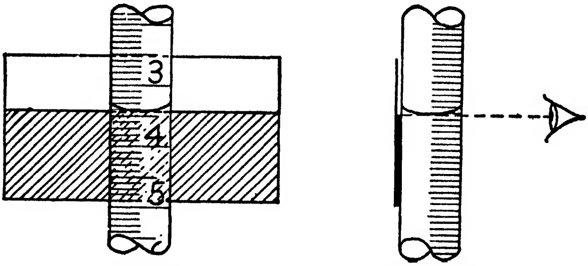

FIG. 31. Illustrating the Use of a Card in Buret Readings.

In the case of all instruments for delivering liquids, the glass must be absolutely clean so that the film of liquid never breaks at any point. Careful attention must be paid to this fact or the required amount of solution will not be delivered. An efficient cleaning solution is made by dissolving powdered sodium bichromate in concentrated sulfuric acid. This mixture must be allowed to stand for some time in the vessel which is being cleaned, and may then be returned to a storage bottle. Fuming nitric acid acts more rapidly, but is disagreeable to handle. In either case, when the acid becomes dilute, the cleaning mixture is no longer effective. A mixture of concentrated sulfuric and fuming nitric acids is even more efficient, but is unpleasant to use.

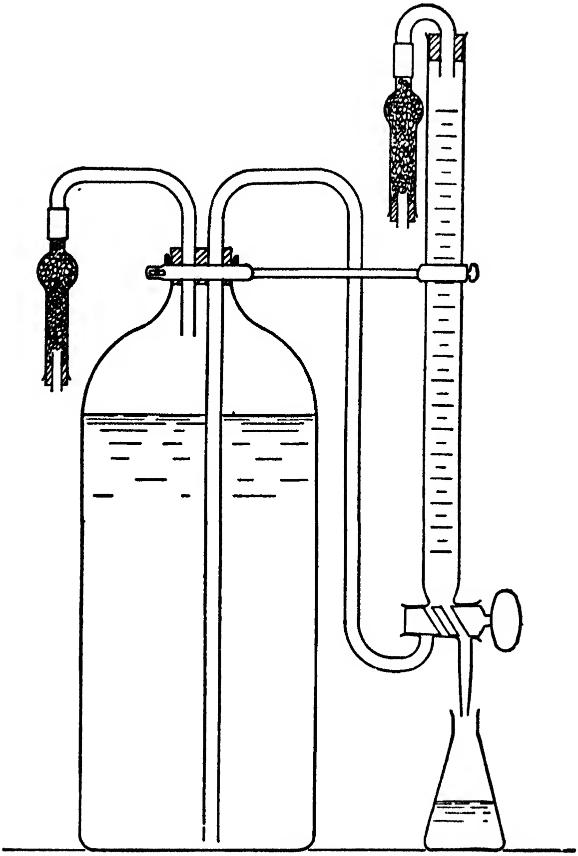

Fig. 32. Storage Bottle for Alkali. The two calcium chloride tubes are filled with ascarite, held in place by cotton or asbestos plugs. The solution is transferred to the buret with the aid of air pressure applied through the calcium chloride tube attached to the bottle, or by suction applied through the guard tube attached to the buret.

Alkaline preparations, such as alcoholic potassium hydroxide and dilute solutions of sodium hydroxide or of trisodium phosphate, remove grease. In these cases, the treatment with the alkaline material is followed by washings with water, acid, and then water a second time. An effective solution is described on pp. 15-16. Acetone is also a useful cleaning agent. To dry glass apparatus, rinse it out with acetone, not with alcohol and ether, and blow or draw air through it.

Alkaline solutions may be protected from the carbon dioxide of the air by an assembly such as that shown in Fig. 32.

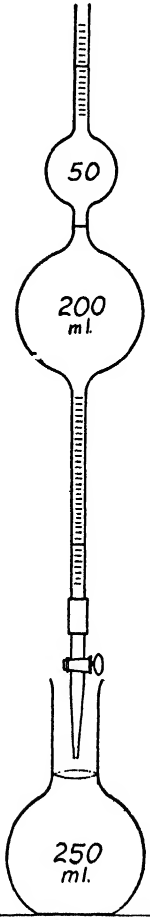

FIG. 33. Morse-Blalock Flask Calibrator.

CALIBRATION OF VOLUMETRIC WARE

It is desirable to have provided a stock of properly calibrated glass apparatus. When this is not feasible, the calibrations of the available apparatus must be checked.

The calibration or testing of apparatus is based upon the true liter, that is, upon the volume occupied by 1 kilogram of water at its temperature of maximum density, 4° C., in vacuo. It is impractical to weigh water in vacuo, and hence the weight of water is found, which when weighed at room temperature under ordinary atmospheric conditions, with brass weights, will occupy a true liter. This can be done by compensating for the temperature difference between the room and the temperature of maximum density, the relative buoyant effect of air on the water and the weights, and the effect of temperature upon the volume of the glass vessel. All of these factors have been taken into account in calculating the final values which are summarized in Table VI, p. 107.

The liter and its subdivisions are derived with the aid of the unit of mass rather than the unit of length; the subdivisions are properly called centiliters, milliliters, etc., instead of cubic decimeters, cubic centimeters, etc. The distinction between 1 liter and 1000 cubic centimeters is so slight that it has no

TABLE VI. WEIGHT OF WATER TO GIVE TRUE LITER AT 20° C.

Temperature, C.	Weight of True Liter in Air, g.	Volume Occupied by 1 g.-ml.	Temperature, C.	Weight of True Liter in Air, g.	Volume Occupied by 1 g.-ml.	Temperature, C.	Weight of True Liter in Air, g.	Volume Occupied by 1 g.-ml.
10	998.39	1.0016	17	997.66	1.0023	24	996.38	1.0036
11	998.32	1.0017	18	997.51	1.0025	25	996.16	1.00385
12	998.23	1.0018	19	997.35	1.0026	26	995.93	1.0041
13	998.14	1.00186	20	997.18	1.0028	27	995.69	1.0043
14	998.04	1.0019	21	997.00	1.0030	28	995.44	1.0046
15	997.93	1.0021	22	996.80	1.0032	29	995.18	1.0048
16	997.80	1.0022	23	996.59	1.0034	30	994.91	1.0051

practical significance in volumetric analysis. One liter equals 1000.028 cubic centimeters. The capacity of modern glassware is usually noted in milliliters (ml.).

Calibration of Apparatus. Flask. This calibration may be done by weighing the water which fills the vessel up to the mark, or, more conveniently, by the use of a Morse-Blalock calibrator (Fig. 33) which is designed to deliver a definite volume of water. Have the flask clean and dry. Place the flask and a weight corresponding to its nominal value (e.g., 250 g. for a 250 ml. flask) on the left pan of a rugged balance that is sensitive to about 5 mg. per scale division. Place weights, shot, or other convenient, dry material on the other pan until equilibrium is established. Now remove the nominal weight from the left pan, and add a weight to compensate for the various corrections: buoyancy of air, etc. For example, if the temperature was 16° C., 250 ml. of water should weigh ¼ of 997.80 g. or 249.45 g. (see Table VI. Hence 250.00 − 249.45 = 0.55 g. should be placed on the left pan so that when equilibrium is reestablished by adding water to the flask, 249.45 g. will have been added. In adding the water, care should be taken not to let drops adhere to the neck of the flask above the level of the water. The final adjustment is made by means of a pipet or capillary tube, after removing drops from the neck of the flask by means of filter paper. The new mark, if one is found, is made by means of a label, and the distance from the original mark to the meniscus is measured and noted.

It is often more convenient to fill the flask exactly to the mark, and from the weight of the water to calculate the volume and mark it on the flask.

Approximate Comparison of Flask and Pipet. A rough check of the volume of one vessel in terms of the other may be obtained as follows: Have ready a clean 50 ml. pipet and a clean, dry 250 ml. volumetric flask; fill the pipet to the mark and empty it five times in succession into the flask (cf. p. 103 for manipulation). If the level does not correspond with the mark on the neck of the flask, paste a label with its upper edge on a level with the bottom of the meniscus. Note the temperature of the water, and measure and note the distance between the original mark and the new one.

Pipet. In volumetric analysis, pipets are calibrated in the following manner to deliver a definite volume. Fill the clean pipet to the mark with distilled water and allow it to deliver into a weighed weighing bottle or a 50 ml. glass-stoppered flask. Reweigh the vessel, and from the weight and temperature of the water calculate the volume delivered, using the data of Table VI, p. 107. If the weight delivered is less than the correct amount, paste a narrow strip of paper vertically above the mark at a position from which it is estimated that more than the correct weight of water will be delivered. Determine the weight delivered from this new mark, calculate a point from which the correct weight should be delivered, and test the correctness of this third mark. If the pipet delivers too much water from the original mark, the second and third marks are placed below the original

TABLE VII. HEIGHT IN MM. CORRESPONDING TO 1 ML. CONTENT FOR VARIOUS DIAMETERS OF TUBES

Inner Diameter of Pipet Tube, mm.	Length that Corresponds to 1 ml. Content mm.	Inner Diameter of Pipet Tube, mm.	Length that Corresponds to 1 ml. Content mm.
2	318	6	35
2.5	204	6.5	30
3	141	7	26
3.5	104	7.5	22.6
4	79	8	19.9
4.5	63	9	15.7
5	51	10	12.7
5.5	42		

one. Measure and note the distance from the original to the correct mark. An alternative method is to find a correction from the weight delivered from the original mark, and to apply this correction whenever the instrument is used. Table VII, p. 108, is useful in calculating the proper position of the mark.

The limits of error for flasks, burets and pipets are:

Flasks

Capacity, ml.	50	100	250	500	1000
Error, ml.	0.05	0.08	0.11	0.15	0.3

Pipets

Capacity, ml.	5	10	25	50	100
Error, ml.	0.01	0.02	0.025	0.05	0.08

Burets

Capacity, ml.	5	10	30	50	100
Error, ml.	0.01	0.02	0.03	0.05	0.10

(U. S. Bureau of Standards, Circular No. 9. For more detailed information see I. M. Kolthoff, Volumetric Analysis, Vol. II, Chap. I, Translation by N. H. Furman. J. Wiley & Sons, Inc., New York.)

Buret. Prior to calibration a buret is cleaned and the stopcock greased with special lubricant. The buret is then filled with water which has come to room temperature and the temperature of the water is noted. The water delivered for convenient intervals, say 5 or 10 ml., is caught in a weighing bottle and weighed. Weights need be observed only to the nearest one hundredth of a gram. It is possible to derive corrections for intervals, as 0-10 ml., 10-20 ml., etc., or total corrections, 0-10 ml., 0-20 ml., etc. A card or other approved device is used in reading the buret; the readings should be estimated to the nearest hundredth of a milliliter. The results should be tabulated; one type of tabulation is given on p. 110.

The volume actually delivered is calculated from the weight delivered; this weight is multiplied by the volume occupied by 1 g. of water at the temperature in question (Table VI, p. 107).

TABLE VIII. CALIBRATION OF A BURET. TEMPERATURE 27° C.

Interval	Reading ml.	Difference in readings	Weights g.	Difference in weights	Volume delivered	Corrections, ml.	Total corrections, ml.
40–50	50.00	10.02	86.29	10.01	10.05	+0.03	+0.07
30–40	39.98	9.97	76.28	9.92	9.96	−0.01	+0.04
20–30	30.01	10.00	66.36	9.98	10.02	+0.02	+0.05
10–20	20.01	9.97	56.38	9.96	10.00	+0.03	+0.03
0–10	10.04	10.01	46.42	9.97	10.01	±0.00	±0.00
Initial	0.03	.....	36.45				

The tabulation is begun at the bottom of a suitably ruled space for convenience in making subtractions.

The calibration is repeated and individual intervals are checked until the corrections agree within 0.02 ml. for each interval. The average total correction values are convenient for use.

REVIEW QUESTIONS AND PROBLEMS

1. Show how HIO_3 may have four different equivalents.

Note: Reduction to ICl is a possibility.

2. Compare the equivalents of $H_4Fe(CN)_6$ in acidimetric and in oxidation reactions.

3. Name two alkaline and four acid substances suitable for primary standards.

4. A pipet delivers 9.90 g. of water at 20° C. when filled to a temporary mark. The inner diameter of the stem is 3 mm. How much higher should the permanent mark be placed in order that the pipet may deliver exactly 10 ml.?

5. What error may be introduced when using a pipet calibrated as above for measuring organic liquids or concentrated solutions?

CHAPTER VII

ACIDIMETRY AND ALKALIMETRY, OR NEUTRALIZATIONS

THEORETICAL CONSIDERATIONS

Acidimetry is the determination of acidic substances by titration and alkalimetry is the corresponding process for basic substances; the two processes, which are neutralizations, make up one of the most important branches of volumetric analysis.

The topic of equivalent weights and the preparation of standard solutions has been discussed in a general way in the preceding chapter; further details are given in the following chapter.

Neutralization. In general the final equilibrium in a process of neutralization depends upon the competition of various substances for hydrogen ions. In aqueous solution the critical question is the effect of other equilibria upon that between water and its ions: $H^+ + OH^- \rightleftharpoons H_2O$.[1] The net result is that the stoichiometric point, or point where equivalent quantities of an acid and a base have been brought together does not necessarily correspond to the same "reaction," or hydrogen-ion concentration as that of pure water.

Hydrogen-ion Concentration and the pH Scale. The equilibrium constant for the ionization of water may be formulated:

$$\frac{[H^+]\,[OH^-]}{[H_2O]} = K,$$

at constant temperature. In any dilute aqueous solution the concentration of non-ionized water is very large, approximately 55.5 molar, and substantially constant. Hence

$$[H^+]\,[OH^-] = \underset{\text{const.}}{[H_2O]K} = K_w$$

---

[1] In understanding the general relationships it is not necessary to write the equation to show the formation of oxonium ion: $2H_2O \rightleftharpoons H_3O^+ + OH^-$.

K_w is the ion-product constant of water. At any given temperature the numerical value of K_w serves as the basis for a scale of acidity. Activity measurements show that the product of the activities of the ions of water varies with the concentrations of salts like KCl, NaCl, etc., but not by a factor of more than 2 up to high concentrations of salt.[1] The constant varies 100-fold from room temperature up to the boiling point, as is shown by the data in the following table.

TABLE IX. ION-PRODUCT CONSTANT OF WATER AT VARIOUS TEMPERATURES.[2]

Temp. °C.	K_w	Temp. °C.	K_w
0	0.12×10^{-14}	50	5.66×10^{-14}
18	0.59×10^{-14}	100	58.2×10^{-14}
25	1.04×10^{-14}		

At room temperature the constant may be assumed to have an approximate value of 10^{-14}, which is used in order to simplify the discussion. In pure water at any temperature:

$$[H^+] = [OH^-] = \sqrt{K_w}$$

For any aqueous solution we need use only one of the quantities $[H^+]$ or $[OH^-]$ to characterize the reaction, since either may be derived when the other is known by the relations: $[H^+] = \frac{K_w}{[OH^-]}$ or $[OH^-] = \frac{K_w}{[H^+]}$. For example, for a solution in which $[H^+] = 1$ molar, $[OH^-] = \frac{K_w}{1} = 10^{-14}$ at room temperature.

For purposes of brevity and convenience as well as for theoretical reasons Sörensen[3] suggested that the exponents with reversed sign be used instead of the hydrogen-ion values themselves. These "hydrogen-ion exponents" constitute the *pH*

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[1] Measurements given by H. S. Harned, Trans. Am. Electrochem. Soc. **51**, 571 (1929).

[2] Kohlrausch and Heydweiler (From Kolthoff and Furman, Potentiometric Titrations, J. Wiley & Sons, Inc.).

[3] S. P. L. Sörensen, Biochem. Z. **21**, 131 (1909).

scale which is related to the values for hydrogen-ion concentration as follows:

$$[\mathrm{H}^+] = 10^{-p\mathrm{H}};\ \text{or}\ \ p\mathrm{H} = \log \frac{1}{[\mathrm{H}^+]};\ \text{or}\ p\mathrm{H} = -\log\,[\mathrm{H}^+].$$

Thus a hydrogen-ion concentration of 10^{-8} corresponds to $p\mathrm{H} = 8$. A quantity $p\mathrm{OH}$ is defined in similar fashion by the relations:

$$[\mathrm{OH}^-] = 10^{-p\mathrm{OH}};\ \text{or}\ p\mathrm{OH} = -\log\,[\mathrm{OH}^-];\ \text{or}\ p\mathrm{OH} = \log \frac{1}{[\mathrm{OH}^-]}\cdot$$

The relation of $[\mathrm{H}^+]$ to $p\mathrm{H}$ and $p\mathrm{OH}$ is indicated in the following scale:

			Acidic Solutions					Pure Water		Alkaline Solutions					
$[\mathrm{H}^+]$	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
$p\mathrm{H}$	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
$p\mathrm{OH}$	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0

For water at any temperature: $p\mathrm{H} + p\mathrm{OH} = pK_w$, and at room temperature $pK_w = 14$. Here pK_w is defined by relations of the same form as $p\mathrm{H}$ and $p\mathrm{OH}$, that is, $\mathrm{K}_w = 10^{-pkw}$. Similar expressions may be used to advantage in handling ionization constants of acids and bases, solubility product constants, etc. The expressions pK_w, pK_a, pK_b, etc., are commonly abbreviated to pW, pA, pB, etc.[1] The reaction of any aqueous solution at room temperature is defined by:

$p\mathrm{H} < 7 < p\mathrm{OH}$ Acidic reaction

$p\mathrm{H} = 7 = p\mathrm{OH}$ Neutral reaction

$p\mathrm{H} > 7 > p\mathrm{OH}$ Alkaline reaction.

The reaction of a solution may be measured quantitatively with the aid of two electrodes which are placed in contact with the solution; one electrode must respond quantitatively to changes in $p\mathrm{H}$. The other electrode is a constant or reference electrode. The electromotive force of the cell is measured by a compensation method. The principle of a suitable experimental assembly is indicated in Fig. 44, p. 204. Another method of measuring $p\mathrm{H}$ is with the aid of the color shown by an appropriate indicator. This method depends upon the electromotive

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[1] See Appendix for a review of logarithmic transformations and for the conversion of various quantities to logarithmic or exponential forms.

force method for its initial fundamental data. If the ionization constants of the reactants are known it is possible to calculate reasonably accurately the course of pH as a titration progresses. Formulae for this purpose are given in Table XXIV, p. 479, in the Appendix. Graphs of pH vs. milliliters of standard solution added will be given in connection with the theory of neutralization in order to illustrate the general relationships.

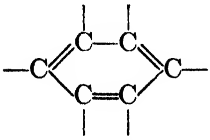
INDICATORS

The electrical method that has been briefly referred to in the preceding section serves as a universal indicator for titrations of all kinds, and it has been used to establish the fundamental facts about the indicators that are commonly used in neutralizations. These are organic substances of weakly acidic or basic character. They show sharp color transformations from colorless to colored forms, or from one colored form to another at definite and rather narrow ranges of pH.

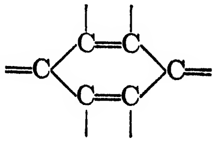
The Theory of Indicator Action. Ostwald attributed the color change to ionization; for an indicator that is an acid, this view might be formulated:

$$\underset{\substack{\text{Acid}\\\text{form}}}{\text{HIn}} \rightleftharpoons \text{H}^+ + \underset{\substack{\text{Alkaline}\\\text{form}}}{\text{In}^-}$$

Phenolphthalein is weakly acidic, and according to this view the undissociated acid is colorless and the anion is red. Similarly for an indicator like methyl orange, which is a very weakly basic substance, $\underset{\substack{\text{Alkaline}\\\text{form}}}{\text{InOH}} \rightleftharpoons \underset{\substack{\text{Acid}\\\text{form}}}{\text{In}^+} + \text{OH}^-$. The alkaline form of methyl orange is yellow and the acidic form red. It is known, however, that changes in structure accompany the color changes, and that the change proceeds through a number of tautomeric and ionic stages for many indicators. The change in color is frequently attributed to a change of one or more groups in the molecule of the indicator from the benzenoid structure:



to the quinoid structure:



or the reverse process.

In spite of the complicated changes that occur it is possible to use Ostwald's simple view to give a quantitative statement of the way in which the color varies with hydrogen-ion concentration. An expression for the equilibrium constant of an indicator that is an acid is: $\frac{[H^+][In^-]}{[HIn]} = K$. The constant, K, is a composite one, or an apparent ionization constant which includes others relating to the tautomeric changes, etc. This equilibrium expression may be written

$$[H^+] = K\frac{[\text{Acidic form}]}{[\text{Alkaline form}]}.$$

This expression makes it clear that if the two forms of the indicator are equally easy to perceive, the color transition should appear at a molar concentration of hydrogen ion that is numerically equal to K. The visual color change is never at a single point on the pH scale, but is spread over a range that depends upon the ease with which the color of one form may be seen in the presence of the other. In the majority of instances slight changes in tint can be perceived over a range of about 2 pH units. In a titration, a single drop of standard solution causes a marked change, or sometimes a complete shift from one color to another. By experiments with fairly large quantities of indicators and with suitable color filters and optical devices it can be shown that both forms of an indicator are present after the titration is started, but to the eye the color appears to change somewhere between the neutralization of 0.1 and 0.9 of the indicator, except in the case of an indicator that has one colorless form; the change then appears as soon as enough of the colored form has been developed to tint the solution. The point of the change with this type of indicator, of which phenolphthalein is an example, depends upon the amount of the indicator that is added. With phenolphthalein, 2 drops of the 1 per cent indicator per given volume of solution changes color at pH 9, whereas with ten times as much indicator in the same volume of solution the change is apparent at pH 8.

The indicator that is selected for a titration must change color at or as nearly as possible at the pH that will prevail at the equivalence point. For the vast majority of analytical titrations the appropriate one of the indicators: Methyl orange, methyl red or phenolphthalein, will serve. It is desirable, however, to have a somewhat wider selection of indicators for use, as is given in Table X, together with the $[H^+]$, $[OH^-]$ and *p*H values of the visual end-points.

TABLE X. SELECTION OF INDICATORS FOR NEUTRALIZATIONS

Indicator	Change Occurs at			Color in Acid Solution	Color in Alkaline Solution	Transition Tint	
	OH^-	H^+	*p*H				
Thymolphthalein...	10^{-4}	10^{-10}	10	colorless	blue	pale blue	Alkaline
Thymol blue (alkaline range)......	10^{-5}	10^{-9}	9	yellow	blue	blue-violet	
Phenolphthalein...	10^{-5}	10^{-9}	9	colorless	red	pale rose	
If high concn...	10^{-6}	10^{-8}	8	colorless	red	pale rose	
Cresol red........	10^{-6}	10^{-8}	8	yellow	red	red	
Bromthymol blue..	10^{-7}	10^{-7}	7	yellow	blue	green	
Bromcresol purple.	10^{-8}	10^{-6}	6	yellow	blue	purplish green	Acid
Methyl red.......	10^{-9}	10^{-5}	5	red	yellow	yellowish red	
Methyl orange....	10^{-10}	10^{-4}	4	red	yellow	orange	
Methyl yellow....	10^{-10}	10^{-4}	4	red	yellow	yellowish orange	
Bromphenol blue..	10^{-10}	10^{-4}	4	yellow	blue	blue-violet	

Litmus is rarely used in titrations owing to the indistinctness of the color change which occurs at about *p*H 7.

If a solution of 0.00001 *N* hydrochloric acid is prepared, it will react barely acid to methyl red, and alkaline to methyl orange or bromphenol blue since the latter would not be affected unless the acid were 0.0001 *N*.

The considerations that are here presented apply to titrations at room temperature. The ionization constants of water, the indicators and of weak acids and bases all shift with temperature. The net effect is that at higher temperatures the changes in *p*H are less abrupt, and many indicators give vague changes or changes that are further from the stoichiometric point than at room temperature. Methyl orange and methyl red, especially the former, should not be used for titrations in hot solutions.

THE THEORY OF NEUTRALIZATION

The following rough classification of acids and bases according to degree of ionization will be used in the subsequent discussion.

The strong, or highly ionized acids and bases, as has been explained in the preceding chapter are apparently completely ionized, though the activity of the ions is in general about 0.95 of the molecular concentration at 0.001 *M* concentration, and about 0.8 at 0.1 molar. The common mineral acids and sodium, potassium, barium and calcium hydroxides and almost all salts are highly ionized.

Weak ("medium weak," "moderately weak") or slightly ionized substances may be defined arbitrarily as acids or bases that have ionization constants, K_a or K_b, respectively, that lie between 10^{-3} and 10^{-8}. Many of the more important ones have constants of the order of 10^{-5}, as is the case both with acetic acid and ammonium hydroxide.

Very weak acids or bases will be defined arbitrarily as those with ionization constants smaller than 10^{-8}. The acids and bases in this class can not be titrated satisfactorily with indicator technique in 0.1 *N* solutions. See Table XXI, Appendix, for numerical values of ionization constants.

The important individual cases of neutralizations will now be considered.

It should be continually borne in mind that a titration is inherently less sensitive the further the *p*H of the stoichiometric point is removed from a *p*H of 7. The exponential nature of the *p*H scale should be recalled and attention should be given to the fact that it requires ten times as much acid to change the *p*H of water or an unbuffered solution from 5 to 4 as would be needed to change the solution from *p*H 6 to 5. Similar considerations apply to the change in *p*OH upon the addition of a base to water or an unbuffered solution.

1. **Neutralization of a Strong Acid with a Strong Base,** or vice versa. In these cases there is a very abrupt change in *p*H at the end of the titration, as is indicated in Figs. 34 and 35. The theoretical end-point or stoichiometric point is at $[H^+] = [OH^-] = \sqrt{K_w}$, or at $pH = pOH = \frac{1}{2}pW = 7$, at room temperature, since at this point the solution contains the ions of a salt like NaCl which does not change the reaction of pure water. Practically, however, the solution will contain carbon dioxide absorbed from the air, so that the *p*H which should be considered in selecting the indicator is more nearly 6. If carbon dioxide were completely excluded a single drop of 0.1 *N* acid or alkali

should change the pH of 100 ml. of 0.1 N NaCl by about 3 units. The practical change is not so pronounced if the solution contains some dissolved carbon dioxide. It is therefore desirable to use methyl red as an indicator in the titration of strong acids with strong bases. Work with solutions more dilute than 0.1 N involves rigid exclusion of carbon dioxide and in extreme cases taking into account the amount of acid or base in the few drops of indicator that are added.

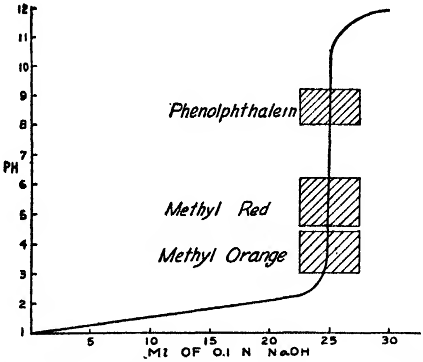


FIG. 34. pH vs. Ml. of 0.1 N NaOH in the Titration of 25 Ml. of 0.1 N HCl. In Figs. 34–40 the shaded blocks show the transition ranges of the indicators.

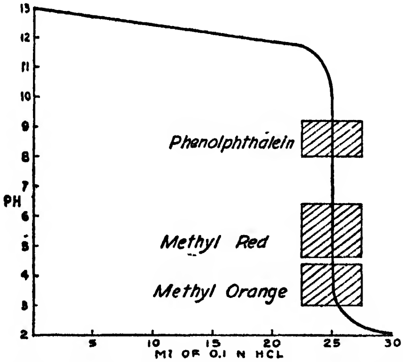


FIG. 35. Graph of pH vs. Ml. of 0.1 N Acid in the Titration of 25 Ml. of 0.1 N NaOH.

2. **Neutralization of a Weak Acid with a Strong Base, or of a Weak Base with a Strong Acid.**

(*a*) *Weak Acid with a Strong Base.* The course of *p*H during a typical titration is indicated in Fig. 36. The change in *p*H near the equivalence-point is by no means as abrupt in this as in the preceding case (1). The *p*H at the equivalence point is greater than 7 (alkaline reaction). Its value depends upon the concentration of the solution and upon the ionization constant of the weak acid. The titration of acetic acid ($K_a = 1.75 \times 10^{-5}$) is a case in point. At the equivalence-point we have a solution of sodium acetate of some particular concentration, *c*. Such a solution reacts slightly alkaline:

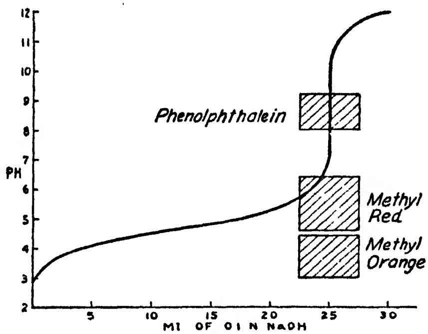


FIG. 36. Graph of *p*H vs. Ml. of Reagent. Titration of 25 ml. of 0.1 *N* Acetic Acid with 0.1 *N* Sodium Hydroxide.

$$Na^+ + C_2H_3O_2^- + \overset{\overset{\displaystyle H_2O}{\downarrow\uparrow}}{H^+ + OH^-} \rightleftharpoons Na^+ + OH^- + HC_2H_3O_2$$

$$\text{or} \qquad C_2H_3O_2^- + \overset{\overset{\displaystyle H_2O}{\downarrow\uparrow}}{H^+ + OH^-} \rightleftharpoons OH^- + HC_2H_3O_2$$

$$\text{In general} \qquad A^- + \overset{\overset{\displaystyle H_2O}{\downarrow\uparrow}}{H^+ + OH^-} \rightleftharpoons OH^- + HA,$$

A^- representing the anion of the weak acid. The equilibrium depends upon the competition of the ions A^- and OH^- for possession of the hydrogen ion. The two equilibria are those for the ionization of water and for the ionization of the acid,

$$[H^+] = \frac{K_w}{[OH^-]} \; (1) \quad \text{and} \quad [H^+] = K_a \frac{[HA]}{[A^-]} \qquad (2)$$

the latter being merely a rearrangement of the ionization expression

$$\frac{[\mathrm{H}^+]\,[\mathrm{A}^-]}{[\mathrm{HA}]} = K_a.$$

The hydrogen-ion concentration must satisfy both (1) and (2), that is, be the same for both expressions at equilibrium. We may then equate the right-hand parts of (1) and (2) to give:

$$\frac{K_w}{[\mathrm{OH}^-]} = K_a\,\frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

which may be rearranged to give:

$$[\mathrm{OH}^-]\,[\mathrm{HA}] = \frac{K_w}{K_a}\,[\mathrm{A}^-] \tag{3}$$

Two simplifying assumptions are now made: (a) that $[\mathrm{OH}^-] = [\mathrm{HA}]$, since these substances are formed in equivalent amounts when the anion reacts with water; and (b) that $[\mathrm{A}^-]$ may be set equal to c, the molar concentration of the salt at the equivalence-point, in spite of the fact that a portion of the anion has combined with hydrogen ion to form the molecule, HA.

The equation (3) then becomes:

$$[\mathrm{OH}^-]^2 = \frac{K_w}{K_a}\,c,$$

or

$$[\mathrm{OH}^-] = \sqrt{\frac{K_w}{K_a} \times c} \qquad (4)^1$$

---

[1] The simplifying assumptions that have been made in deriving (4) and the analogous formula for the weak base-strong acid case apply to a very good degree of approximation for the cases that are of most practical interest, where K_a and K_b are between 10^{-4} and 10^{-6}. The assumption that $[A^-] = c$ is less valid the greater the degree of hydrolysis, that is, the less is K_a and the smaller is c. On the other hand the assumption that $[\mathrm{HA}] = [\mathrm{OH}^-]$ becomes more valid with increasing degree of hydrolysis. Hence the next approximation to use in cases not satisfied by equation (4) is

$$[\mathrm{OH}^-]^2 = \frac{K_w}{K_a}\,(c - [\mathrm{OH}^-])$$

If desired, equation (4) may be transformed by substituting $\frac{K_w}{[\mathrm{H}^+]}$ for $[\mathrm{OH}^-]$ and taking the negative logarithm of both sides of the equation. It then has the form:

$$p\mathrm{H} = \tfrac{1}{2}p\mathrm{W} + \tfrac{1}{2}p\mathrm{A} + \tfrac{1}{2}\log c.$$

The use of equation (4) may be illustrated by calculating the pH at the equivalence-point in the titration of 0.1 N acetic acid of $K_a = 1.75 \times 10^{-5} = 10^{-4.76}$, with 0.1 N sodium hydroxide. Equal volumes of the two solutions react and the concentration of the sodium acetate is therefore 0.05 N at equivalence.

$$[\mathrm{OH^-}] = \sqrt{\frac{10^{-14}}{10^{-4.76}}\,0.05} = \sqrt{\frac{10^{-14}\,10^{-1.3}}{10^{-4.76}}} = \sqrt{\frac{10^{-15.3}}{10^{-4.76}}}$$

$$= \sqrt{10^{-10.54}} \qquad = 10^{-5.27}$$

Hence $p\mathrm{OH} = 5.27$ or $p\mathrm{H} = 14 - 5.27 = 8.73$. As may be seen from Table X, either phenolphthalein or thymol blue would be a suitable indicator.

(*b*) *Weak Base with Strong Acid.* The course of pH during a typical titration of this class is shown in Fig. 37. As in (*a*) the change in pH is not abrupt near the end-point as compared with the strong acid-strong base case. The end-point in this case lies in a region of pH less than 7. The calculation of the pH at the end-point is based on the same type of reasoning that has been given for the converse case. Considering the reaction:

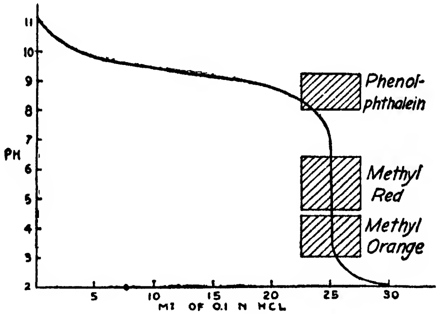


FIG. 37. Graph of pH vs. Ml. of 0.1 N HCl in the Titration of 25 Ml. of 0.1 N Ammonium Hyroxide.

$$\mathrm{B^+ + H^+ \overset{\displaystyle H_2O}{\overset{\downarrow\;\uparrow}{+}} OH^- \rightleftharpoons H^+ + BOH,}$$

$\mathrm{B^+}$ being the cation of a weak base, it is clear that the solution contains an excess of hydrogen ions at equilibrium. The equilibria involved are

$$[\mathrm{OH}^-] = \frac{K_w}{[\mathrm{H}^+]} \quad (5) \quad \text{and} \quad [\mathrm{OH}^-] = K_b\frac{[\mathrm{BOH}]}{[\mathrm{B}^+]} \qquad (6)$$

the latter being a rearrangement of the expression for the ionization of the weak base. The two relations have to be satisfied in the same solution, hence the right-hand sides of (5) and (6) may be equated to give:

$$\frac{K_w}{[\mathrm{H}^+]} = K_b\frac{[\mathrm{BOH}]}{[\mathrm{B}^+]}. \qquad (7)$$

Again making assumptions (*a*) that $[\mathrm{H}^+] = [\mathrm{BOH}]$ and (*b*) that $[\mathrm{B}^+] = c$, where c is the molar concentration of the salt that is formed, at the equivalence-point, equation (7) becomes

$$[\mathrm{H}^+]^2 = \frac{K_w}{K_b}c, \quad \text{or} \quad [\mathrm{H}^+] = \sqrt{\frac{K_w}{K_b}c}. \qquad (8)^1$$

Illustration of the use of equation 8. If 0.2 N ammonium hydroxide is titrated with 0.2 N hydrochloric acid the concentration of ammonium chloride at the equivalence point is 0.1 N. The ionization constant, $K_b = 1.75 \times 10^{-5} = 10^{-4.76}$, for ammonium hydroxide. Hence

$$[\mathrm{H}^+] = \sqrt{\frac{K_w}{K_b}c} = \sqrt{\frac{10^{-14}}{10^{-4.76}}10^{-1}} = \sqrt{10^{-10.24}} = 10^{-5.12}$$

The pH at the end of the titration is 5.12; methyl red is the appropriate indicator.

If the graphs of pH vs. milliliters of reagents are determined for weaker and weaker acids or bases, a series of curves similar to those shown in Figs. 38 and 39 is obtained. The change in pH near the end-points becomes less and less marked. With extremely weak acids like hydrocyanic, boric, etc., or extremely weak bases of constants of the order of 10^{-10} it is not possible to titrate with an accuracy greater than 1-2 per cent even though the substance titrated and the reagent are both 1 normal.

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[1] The same limitations apply to the use of equation (8) as have been indicated for equation (4) in footnote (1) on p. 120. Also by taking the negative logarithm of both sides of equation (8) it can be seen that the equation is equivalent to: $p\mathrm{H} = \frac{1}{2}p\mathrm{W} - \frac{1}{2}p\mathrm{B} - \frac{1}{2}\log c$.

3. Titration of a Weak Acid with a Weak Base, or vice versa. This type of titration is avoided in practical volumetric analysis.

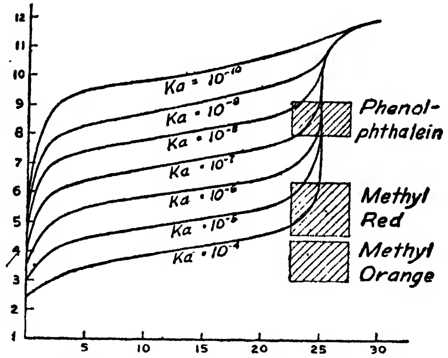

FIG. 38. Graphs Showing the Course of pH vs. Ml. of 0.1 N NaOH, in the Titration of 25 Ml. Portions of Various Acids of the K_a Values Indicated (10^{-4}, 10^{-5}, 10^{-6}, etc.).

There is no sharp change in pH with small additions of acid or base near the equivalence-point. The theoretical pH lies close to 7 at the end-point and is independent of the dilution as a first approximation; the $[H^+]$ may be calculated from the equation:[1]

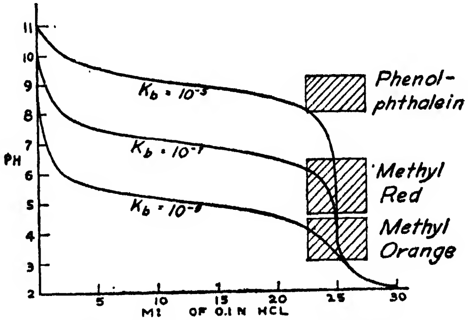

FIG. 39. Graphs Showing the Course of pH vs. Ml. of 0.1 N HCl in the Titration of 25 Ml. Portions of Bases of K_b 10^{-5}, 10^{-7} and 10^{-9}.

$$[H^+] = \sqrt{\frac{K_w K_a}{K_b}}$$

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[1] See I. M. Kolthoff, Volumetric Analysis (Transl. by N. H. Furman), J. Wiley & Sons, Inc., Vol. 1, p. 27, for a derivation of this formula.

4. The Titration of Polybasic Acids or Bases, or Mixtures of Acids or Mixtures of Bases. If the ionization constants of the different substances, or of the various stages of the same substance are sufficiently different in order of magnitude, it may be possible to observe a succession of end-points in the same solution, with appropriate indicators, or to titrate to various end-points using separate portions of the solution of the mixture for the titrations with different indicators. Phosphoric acid, for example, behaves, when titrated, like a mixture of three acids of widely different strengths. The constants are:

Process	Constant
$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$\frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]} = K_1 = 1.1 \times 10^{-2}$
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{=}$	$\frac{[H^+]\,[HPO_4^{=}]}{[H_2PO_4^-]} = K_2 = 7.5 \times 10^{-8}$;
$HPO_4^{=} \rightleftharpoons H^+ + PO_4^{\equiv}$	$\frac{[H^+]\,[PO_4^{\equiv}]}{[HPO_4^{=}]} = K_3 = 5 \times 10^{-13}$.

One-third of the total replaceable hydrogen may be titrated rather sharply using methyl orange or methyl yellow as an indicator. If phenolphthalein is used, the color change comes after two thirds of the replaceable hydrogen has been titrated. These changes are shown graphically in Fig. 40. The last third of the hydrogen of phosphoric acid is so slightly ionized and the constant is so near that of water that no indicator will serve to show any change. To state the matter in another way, a solu-

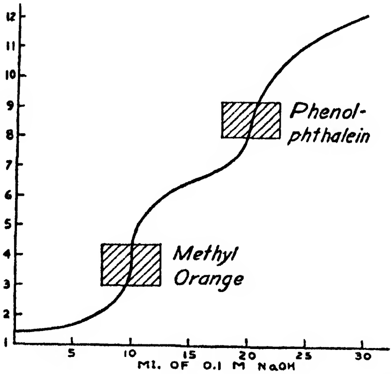

FIG. 40. The Course of pH during the Titration of 30 Ml. of 0.1 Molar Phosphoric Acid with 0.1 N Sodium Hydroxide.

tion of trisodium phosphate, prepared in the dry way, is not distinguishable with indicators from an equivalent mixture of sodium hydroxide and disodium phosphate, Na_2HPO_4. The last third of the hydrogen of phosphoric acid may be titrated fairly accurately if neutral calcium chloride is added after two-thirds of the total hydrogen has been replaced, in order to precipitate the phosphate and liberate the hydrogen ion: $2Na_2HPO_4 + 3CaCl_2 = Ca_3(PO_4)_2 + 4NaCl + 2HCl$.

In general there is a limiting ratio of the various ionization constants if one acid or one stage of an acid is to be titrated sharply in the presence of others. If a precision of 1 per cent is desired, the largest constant must be at least 10,000 times as large as the next constant if the various acids are present in equivalent amounts.[1]

It is possible to titrate a strong acid, or weak acids like acetic, formic, benzoic, etc., in the presence of an extremely weak acid like boric. Table XXI in the Appendix serves to indicate the possibilities of making a differential titration of one acid in the presence of others.

Analogous considerations apply to the titration of a mixture of bases with a strong acid.

Acids and Salts, or Bases and Salts. The titration of a mixture of a highly ionized acid or base, when mixed with a salt derived from a weak acid or base, follows the same rules that hold for the titration of the weak acid or base from which the salt is derived. For example, ammonia is frequently distilled into a standard solution of hydrochloric or sulfuric acid. The solution is then titrated back with alkali to find how much of the acid has combined with ammonia. The indicator must be the one corresponding to the hydrolysis of ammonium chloride or ammonium sulfate in the solution in question.

5. **Titration of Solutions of Hydrolyzed Salts.** *Displacement Titrations.* If a salt of the type that may be derived from an extremely weak acid, as for example, borax ($Na_2B_4O_7$), sodium or potassium carbonate, potassium cyanide, etc., or of the

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[1] If the acids are not present in equivalent amounts, the differences between the constants must be greater for the same accuracy when the weaker acid is present in the higher concentration. See I. M. Kolthoff, Volumetric Analysis, Vol. I, p. 36 (Transl. by N. H. Furman), J. Wiley & Sons, Inc.

reverse type, like aluminum chloride, aniline hydrochloride ($C_6H_5NH_2 \cdot HCl$), etc., is titrated with a strong acid for the first, or a strong base for the second type, the weak acid or base, respectively, is displaced completely, as for example:

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3,$$

$$\text{or} \quad C_6H_5NH_2 \cdot HCl + NaOH = NaCl + H_2O + C_6H_5NH_2.$$

In a titration of this type the pH at the end-point can be calculated if the ionization constant of the acid or base that is displaced is known. In the illustrations that have been given the constants for boric acid or for aniline would be needed.

Illustration. The constant, K_b, for aniline is 3.5×10^{-10}. If a 0.2 N solution of aniline hydrochloride were titrated with 0.2 N sodium hydroxide, the concentration of free aniline at the equivalence point would be 0.1 molar. The constant for a base,

$$K_b = \frac{[B^+]\,[OH^-]}{[BOH]}$$

may be used by making simplifying assumptions, namely that $[OH^-] = [B^+]$, and that the concentration of the base, [BOH], is not significantly altered by the slight amount of ionization. The formula may be used in the simplified form:

$$[OH^-]^2 = K_b[BOH]; \quad \text{or} \quad [OH^-] = \sqrt{K_b[BOH]}.$$

In the present case

$$[OH^-] = \sqrt{3.5 \times 10^{-10} \times 10^{-1}} = \sqrt{10^{-10.46}} = 10^{-5.23}.$$

That is pOH = 5.23 or pH = 8.77. Phenolphthalein would be a suitable indicator for this titration.

The most important single instance of displacement titration is probably that of the titration of the solution of a carbonate with an acid. The carbonic acid which is displaced has two stages of ionization with constants of very different magnitude:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-, \quad K_1 = \frac{[H^+]\,[HCO_3^-]}{[H_2CO_3]} = 3.04 \times 10^{-7};$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^=, \quad K_2 = \frac{[H^+]\,[CO_3^=]}{[HCO_3^-]} = 4 \times 10^{-11}.$$

At the end of the titration:

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl,$$

the reaction is that of a solution of bicarbonate as affected very slightly by the ions of the neutral salt, NaCl. *The reaction of sodium bicarbonate:* The expression for $[H^+]$ that may be easily derived from the ionization constants is

$$[H^+] = \sqrt{\frac{K_1K_2c}{K_1 + c}},$$

c being the concentration of the sodium bicarbonate. Since K_1 is usually of the order of one millionth or less of the value of c, the expression may be simplified to: $[H^+] = \sqrt{K_1K_2}$, as a first approximation. That is, for the titration to the bicarbonate stage

$$[H^+] = \sqrt{3.04 \times 10^{-7} \times 4 \times 10^{-11}} = \sqrt{10^{-16.92}} = 10^{-8.46}.$$

This is a pH 8.46, which is in the range of phenolphthalein. The end-point is not very sharp, and is often inexact due to escape of carbon dioxide caused by a local excess of acid. At 0° C. the change is sharper and more exact; presence of excess of sodium chloride sharpens the change. The titration to this stage is important in determining a small amount of carbonate in the presence of a large excess of sodium or other hydroxide.

After the phenolphthalein is decolorized at the bicarbonate stage another indicator may be added and the titration carried to the displacement of the carbonic acid:

$$NaHCO_3 + HCl \rightleftharpoons NaCl + H_2CO_3.$$

An approximate calculation of the pH at the end-point may be made for any specific case.

Illustration. At the end of the titration of 0.2 M $NaHCO_3$ with 0.2 M HCl, the concentration of H_2CO_3 should be 0.1 M if no loss occurs by escape of CO_2. Since the first stage of the ionization of carbonic acid is moderate and the second stage almost vanishingly small, the $[H^+]$ may be derived from K_1, making the simplifying assumption that $[H^+] = [HCO_3^-]$. Then

$$[H^+] = \sqrt{K_1[H_2CO_3]} = \sqrt{3.04 \times 10^{-7} \times 10^{-1}} = \sqrt{10^{-7.52}}$$
$$= 10^{-3.76};$$

or pH = 3.76. This calculation indicates that methyl orange is the proper indicator, which is correct. The calculation has neglected the ionization of HCO_3^-. In a titration some carbon dioxide escapes so that a more refined calculation is not justifiable here. With tenth normal solutions the change is not very sharp, and therefore a reference solution is prepared with the same *p*H that is expected at the end-point and of the same volume and concentration of indicator as the solution to be titrated.

THE CHOICE OF AN INDICATOR FOR A NEUTRALIZATION

In general there are two simple ways to select the right indicator for an unfamiliar case: (1) The *p*H to be expected at the equivalence-point is calculated, and an indicator that changes at or as near as possible to the calculated point is selected. If several indicators are available their performance may be tested with standardized solutions. In the following table is given a brief summary of the method of finding $[H^+]$ or $[OH^-]$ at the equivalence-point of any type of titration.

Formulas for Calculating $[H^+]$ or $[OH^-]$ at Equivalence-points.

Kind of Titration	*Formula*[1]
(1) A strong acid with a strong base, or vice versa. (If a salt of a weak acid, or base is present in the solution the appropriate one of cases (2) or (3) applies.)	Theory: $[H^+] = [OH^-] = \sqrt{K_w}$ Practice: $[H^+] = \sim 10^{-6}$ if carbon dioxide is present.
(2) A moderately weak acid with a strong base. $K_a = 10^{-3}$ to 10^{-8}.	$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot c}$
(3) A moderately weak base with a strong acid. $K_b = 10^{-3}$ to 10^{-8}.	$[H^+] = \sqrt{\frac{K_w}{K_b} \cdot c}$
(4) Salt of a very weak acid, of K_a about 10^{-10} titrated with a strong acid.	$[H^+] = \sqrt{K_a\,[HA]}$
(5) Salt of a very weak base, of $K_b = 10^{-10}$, titrated with a strong base.	$[OH^-] = \sqrt{K_b\,[BOH]}$

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[1] If desired these formulas may be converted into their equivalent forms in terms of *p*H which are for the various cases: (1) $pH = pOH = \frac{1}{2}pW$; practically $pH = \sim 6$.

(2) $pH = \frac{1}{2}pW + \frac{1}{2}pA + \frac{1}{2}\log c$.

(3) $pH = \frac{1}{2}pW - \frac{1}{2}pB - \frac{1}{2}\log c$.

(4) $pH = \frac{1}{2}pA - \frac{1}{2}\log [HA]$.

(5) $pH = pW - \frac{1}{2}pB + \frac{1}{2}\log [BOH]$.

(2) A second procedure is to prepare from pure materials the mixture that will be present at the equivalence-point of the titration. For cases (2) and (3) in the preceding table pure salts would be dissolved to form solutions of the concentrations that would occur at the equivalence-points. If, for example, it is desired to find appropriate indicators in the titration of 1 *M*, 0.1 *M* and 0.01 *M* benzoic acid with 1, 0.1 and 0.01 *M* sodium hydroxide solutions, respectively, pure sodium benzoate would be dissolved in pure water to form 0.5, 0.05, and 0.005 *M* solutions respectively. It frequently happens that a single indicator will not serve for titrations of the same two substances at several dilutions. In displacement titrations (cases (4) and (5) in the table), the mixture would contain the salt and the weak acid or base in appropriate concentrations. For example, if an indicator is to be chosen for the titration of 0.5 *M* sodium borate with 0.5 *M* hydrochloric acid, a solution 0.25 *M* in both sodium chloride and boric acid would be prepared. (Note: Boric acid, H_3BO_3 may, for this purpose, be regarded as a mono-acid $HBO_2 \cdot H_2O$). In any case the prepared solution may be used in two ways: (*a*) The *p*H may be measured by any suitable method, and the appropriate indicator then selected using a table such as Table X, on p. 116. (*b*) If the *p*H is not determined, portions of the prepared solution are tested with various indicators present, by titrating back and forth with standard acid and alkali to find out whether the change is sharp.

BUFFER MIXTURES

Buffers or buffer systems are compounds or mixtures that have the power of maintaining the *p*H of a solution within a narrow range when slight amounts of acid or alkali are added to it or when it undergoes considerable dilution. The theory of this regulation of the *p*H range by such systems is most clearly understood from the form of the titration graphs of weak acids and of weak bases (Figs. 38 and 39). It will be noted that the central regions of the curves shown in Figs. 38 and 39 are all rather flat, and that the *p*H changes by only 2 units between the point at which one-tenth of the substance has been neutralized and the point at which the titration is nine-tenths complete. It is also evident from an inspection of the graphs that a half-titrated mixture, that is, one with equivalent amounts of a weak acid and its salt, or a weak base and its salt, will require more acid or base to change its *p*H by 1 unit in *either* direction than will any other mixture represented by the graph of this titration. The other mixtures will be less effective in one direction or the other.

A distinction should be made between the *p*H level at which a buffer operates, and the capacity of the buffer to absorb or offset changes in *p*H. The level at which a buffer operates is determined by the ionization constant of the weak acid or base that is used, and the ratio of concentrations of acid and its salt, or base and its salt, respectively. The common ion effect is the important factor in maintaining the *p*H at a given level. The buffer capacity depends upon the total concentration of the buffer mixture. For example, it would take ten times as much acid or base to change by one unit the *p*H of a mixture molar in both acetic acid and sodium acetate as would be required to produce a change of 1 *p*H unit in a mixture that is tenth molar in these substances.

Buffer mixtures are used in analytical chemistry to maintain the *p*H value of the solution in an optimum range during precipitations, oxidation-reduction processes, or other operations, or for purposes of measuring *p*H with the aid of indicators. For example, the acid that is generated in a reaction like: $ZnSO_4 + H_2S \rightleftharpoons \downarrow ZnS + H_2SO_4$ may be sufficient to prevent the complete precipitation of the zinc in the form of zinc sulfide.[1] If the solution is buffered by adding formic acid and ammonium formate, the sulfuric acid that is formed during the precipitation is absorbed by the process: $2H^+ + SO_4^{--} + 2NH_4^+ + 2HCO_2^- \rightleftharpoons 2H_2CO_2 + 2NH_4^+ + SO_4^{--}$. The ionization of the formic acid is repressed and regulated by the presence of formate ions derived from the ammonium formate. If, on the other hand, a little sodium hydroxide were added to a mixture of ammonium formate and formic acid, it would be neutralized to form sodium formate. The hydrogen ions that are momentarily used up in this way are immediately replaced by ionization of some of the undissociated formic acid to yield hydrogen and formate ions. The regulating action has involved

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[1] A further discussion of this process is to be found on pp. 452, 453.

in it the common-ion effect, neutralization, and the existence of a reservoir of non-ionized acid or base.

The fact that the hydrogen-ion concentrations of the various buffer mixtures that may be prepared from any given acid and, for example, its sodium salt, are not affected by diluting them may be understood by rewriting the expression for the ionization constant of an acid in the form: $[\mathrm{H}^+] = K_a \frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$. In a mixture of the acid and its sodium salt, the concentration of the anion, A^-, is determined by that of the sodium salt in the mixture, for this salt is completely ionized, and the amount of the anion derived from the slight ionization of the acid is negligible compared with that derived from the salt. Assuming that the activity of the anions is equal to the concentration of the salt,

$$[\mathrm{H}^+] = K_a \frac{[\mathrm{Acid}]}{[\mathrm{Salt}]}.$$

For any one ratio of moles of acid to moles of salt, e.g., 1 : 10, 1 : 1, 10 : 1 dilution has no effect, since the total volume, V, cancels out:

$$[\mathrm{H}^+] = K_a \frac{\frac{\text{Moles acid}}{V}}{\frac{\text{Moles salt}}{V}}.$$

Exactly similar considerations apply in case of a mixture of a base and its salt, as for example ammonium hydroxide and ammonium chloride. Here

$$[\mathrm{OH}^-] = K_b \frac{\frac{\text{Moles of base}}{V}}{\frac{\text{Moles of salt}}{V}}.$$

From these considerations it is evident that the optimum buffer of any desired hydrogen-ion concentration is prepared by finding an acid of K_a numerically equal to the hydrogen ion concentration desired, i.e., an acid of $K_a = 10^{-5}$ if the desired $[\mathrm{H}^+]$ is 10^{-5}, or pH 5; or by finding a base that has a K_b value numerically equal to the $[\mathrm{OH}^-]$ that is desired. The mixture of the acid and its sodium salt in equimolar ratio, or of the base and its chloride in equimolar ratio will produce a buffer of the reaction desired. The buffer mixture is added to a solution to make a total concentration that will offset the expected development of acid or alkali as the analytical process proceeds.

Although the optimum mixture for any system is the equimolar mixture of an acid or a base and one of its suitable salts, one may prepare a series of several buffer mixtures differing by any convenient *p*H spacing, as, for example, by 0.2 *p*H unit in colorimetric work, by using the acid and its salt or the base and its salt in molar ratios other than 1 : 1. For example, mixtures of acetic acid and sodium acetate in various ratios may be used to prepare buffer mixtures of *p*H between 3.8 and 5.6 at any convenient spacing.

For mixtures 0.1 molar in total acetate[1] *p*H as a function of ratio of moles of acid to moles of salt is:

Sodium acetate, *M*	0.02	0.03	0.04	0.05	0.06	0.07	0.08
Acetic acid, *M*	0.08	0.07	0.06	0.05	0.04	0.03	0.02
*p*H	4.11	4.34	4.52	4.69	4.86	5.05	5.28

And for mixtures 1.0 molar in total acetate:

Sodium acetate, *M*	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Acetic acid, *M*	0.8	0.7	0.6	0.5	0.4	0.3	0.2
*p*H	4.03	4.26	4.46	4.65	4.83	5.04	5.28

These two sets of values serve to show the effect of tenfold dilution upon six particular buffer mixtures of the acetic acid-acetate series. Between 15° and 25° the *p*H of a mixture 0.05 molar in both acetic acid and sodium acetate varies by less than 0.01 *p*H unit.

Mixtures of primary and secondary potassium phosphate (KH_2PO_4 and K_2HPO_4) give the *p*H values that would be expected from the titration curve of phosphoric acid (Fig. 40). In any case of this type we are dealing essentially with a process that is analogous to the acetic acid-acetate case. The salt KH_2PO_4 is highly ionized and the potassium ions have little effect upon the ionization of the ion $H_2PO_4^-$. The essential process is: $H_2PO_4^- \rightleftharpoons$

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[1] These data are obtained by interpolating results given by A. A. Green, J. Am. Chem. Soc. **55**, 2331 (1933). In this paper data are given for intervals of 0.1 *p*H unit and for total acetate concentrations up to 2.0 *M*. A similar convenient table is given in this paper for the system KH_2PO_4—K_2HPO_4 up to 2.0 molar phosphate, covering buffers in the range *p*H 5.3–7.7.

$H^+ + HPO_4^{=}$. The second constant, K_2, for phosphoric acid applies to this process. The addition of K_2HPO_4 represses this ionization just as the addition of sodium acetate represses that of acetic acid. The ionization of $HPO_4^{=}$ into hydrogen and phosphate ions occurs to such an extremely slight extent that it may be ignored, and hence $[H^+] = K_2 \frac{[KH_2PO_4]}{[K_2HPO_4]}$ gives an approximate expression for the $[H^+]$ of these mixtures.[1]

Buffer Mixtures and *p*H Measurement. The *p*H values for carefully prepared buffer mixtures are established in the first instance by electrochemical measurement. After the data have been acquired for particular mixtures, a standard series of buffer mixtures may be prepared at will from carefully purified buffer salts and from standard solutions of acids or bases. Data on the preparation of such mixtures are given in handbooks on chemistry or in books on hydrogen-ion concentration (see literature summary, Appendix, secs. F and M). Suppose that buffers with *p*H values 5.3, 5.4, 5.5.......6.8 have been prepared. Then 10 ml. of each buffer plus a suitable number of drops of an indicator covering this range, as for example bromcresol purple, are placed in a series of 16 similar tubes. The same number of drops of indicator and 10 ml. of the solution to be tested are placed in a similar tube and mixed well. If the color of the solution in the latter tube lies between the colors in any two of tubes of the standard series, the *p*H has been determined as being within a particular tenth of a unit, as for example between 6.2 and 6.3. There are many modifications of colorimetric technique that may be used in the determination of *p*H. Some of these involve the preparation of durable liquid or glass standards which match the color given by an indicator at a definite *p*H; others involve the viewing of the acid and alkaline forms of the indicator in separate solutions of varying depths or at previously determined concentrations to duplicate the color that would be given by the indicator at known *p*H. The reader is referred to books on Hydrogen-ion Concentration for details regarding these methods.

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[1] The article by Green that has been cited gives details of the correction of this simple expression for activity effects.

REVIEW QUESTIONS AND PROBLEMS

1. (a) Transform $[OH^-] = 3.5 \times 10^{-5}$ into pH. (b) Convert $p\text{H} = 3.8$ into $[H^+]$; (c) Convert $[H^+] = 0.2$ into pH. Transform each of the quantities in (a-c) into pOH units. Ans. (a) 9.5; (b) 1.6×10^{-4}; (c) 0.7 : pOH 4.5; 10.2; and 13.3.

2. If an indicator has a constant K_a of 10^{-9}, what will be the pH of the color change, (a) if the colors of the two forms are equally brilliant, and (b) if one part of the alkaline form can be readily distinguished in the presence of 10 parts of the acid form? Ans. (a) pH 9; (b) pH 8.

3. What indicator would be selected for each of the following cases: (a) Titration of a 1.0 M base of $K_b = 10^{-7}$ with 1. M hydrochloric acid. (b) As in (a) but with solutions 0.1 M; (c) For the titration of a 0.5 molar solution of an acid of constant $K_a = 10^{-6}$ with 0.5 M sodium hydroxide.

4. How much phosphoric acid is required to neutralize 40 g. of sodium hydroxide, (a) with phenolphthalein as indicator and (b) with methyl orange as indicator. What is the ratio of the equivalent weight to the molecular weight of phosphoric acid in each of these cases?

5. Given the ionization constant of cinnamic acid, $K_a = 3.7 \times 10^{-5}$, calculate (a) the $[H^+]$, and (b) the pH at the end-point in the titration of a 1.0 N solution of the acid with 1.0 N sodium hydroxide. (c) Select a suitable indicator. Ans. (a) 8.9×10^{-10}; (b) 9.05; (c) Thymol blue or phenolphthalein.

6. Repeat the calculations required in problem 5, (a) for a 0.1 N solution of cinnamic acid titrated with 0.1 N sodium hydroxide, and (b) for 0.01 solutions of the acid and the alkali. Note the indicators that would be satisfactory for these titrations.

7. Calculate the pH at the end of the titration of 25 ml. of 0.25 N ammonium hydroxide with 0.25 N hydrochloric acid. Use 1.75×10^{-5} for the ionization constant of the former.

8. If ammonia is distilled into 50 ml. of 0.1 N hydrochloric acid, neutralizing half of the acid, calculate the pH at the end of the titration of the remaining acid with 0.1 N sodium hydroxide. Ans. $p\text{H} = 5.36$ (or 5.4 rounded).

9. (a) Calculate the pH of the solution in the titration of an acid ($K_a = 5 \times 10^{-7}$), the concentration of the salt formed being 0.01 M. (b) What indicator would be selected? (c) Would the end-point be a sharp one? Reasons?

10. If an indicator that changed at pH 6 was used in the titration of 0.5 N acetic acid with 0.5 N strong base, calculate (a) the decimal fraction of the acid neutralized, and (b) the per cent of the original acid remaining at the point of indicator change. Ans. (a) 0.946; (b) 5.54.

11. Solve the questions similar to those in (10) for an indicator which changes at pH 7 if used in the titration of 0.5 N ammonia with 0.5 N hydrochloric acid.

12. Taking the ionization constant of ammonium hydroxide as 1.75×10^{-5}, calculate the pH when 20 per cent of a 0.1 N solution has been neutralized.

13. Calculate the pH of a 0.2 M solution of a moderately weak monobasic acid ($K_a = 2 \times 10^{-5}$) which is 0.85 M in the potassium salt of the acid.

14. Given the ionization constant of aniline, $K_b = 3.5 \times 10^{-10}$, calculate for a 0.1 M solution of the base: (a) $[OH^-]$; (b) the pH; (c) the degree of ionization, α, and (d) the per cent of ionization (assuming that $1 - \alpha$ may be set equal to 1).

15. How many ml. of 0.1 N sodium hydroxide must be added to 1 liter of water to give a pH of 9 (i.e. to color phenolphthalein)? How many ml. of 0.1 N hydrochloric acid to change the pH of 1 liter of water to 4 (methyl orange transition)? Assume complete ionization of the acid and the base.

16. Calculate the pH at the mid-point of the titration of acetic acid in the following cases: (a) 2 N acid with 2 N sodium hydroxide; (b) 0.2 N acid with 0.2 N sodium hydroxide; (c) 0.02 N acid with 0.02 N sodium hydroxide. Point out the significance of these results. (d) Calculate the pH at the end of each of the three titrations (a-c).

17. Calculate the pH of a mixture of equal volumes of 0.1 M KH_2PO_4 and 0.1 M K_2HPO_4, the former being regarded as a monobasic acid. Ans. $p\text{H} = 7.13$.

18. In what ratios would the solutions mentioned in (17) be mixed to give buffers of the following pH values, respectively: 6.4; 6.8 and 7.2?

19. Calculate the theoretical pH at the end-point of the titration of 50 ml. of 0.5 M pyridine hydrochloride with 0.5 M sodium hydroxide. K_b for pyridine is 1.25×10^{-9}. Ans. 9.25.

CHAPTER VIII

ACIDIMETRY AND ALKALIMETRY. PROCEDURES

PREPARATION OF A STANDARD ACID

A standard solution of an acid may be prepared by weighing a definite amount of a primary standard, such as benzoic acid, $HC_7H_5O_2$; succinic acid, $H_2C_4H_4O_4$; potassium acid phthalate, $KHC_8H_4O_4$; sulfamic acid, HSO_3NH_2; oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, or even an aqueous solution of hydrochloric acid if its exact composition is known. Of the crystalline compounds, potassium acid phthalate is preferable, for it has a high equivalent weight, 204.22, is anhydrous, is not hygroscopic or deliquescent, can be dried at 110° C., is easily obtained pure, and is readily soluble in water. A 0.1 *N* solution of the phthalate contains 20.422 g. per liter. Potassium acid iodate, $KIO_3 \cdot HIO_3$, although not easily obtained pure, has the same advantages, and in addition acts as a strong acid so that various indicators can be used.[1] Benzoic acid is also satisfactory, but is sparingly soluble in water. Succinic acid is sometimes used, but must be dried below 100° C. to avoid formation of succinic anhydride; it is best dried over calcium chloride. A 0.1 *N* solution of this acid contains 5.9044 g. per liter. Oxalic acid cannot be dried by simple heating without losing water of crystallization.[2] Solutions of organic acids have two disadvantages: they decompose after a few days, due to bacterial action, and they are weak acids, and therefore can be titrated only with strong bases. Either hydrochloric acid or sulfuric acid is preferable. They are strong acids and should be prepared in any case, using, if necessary, potassium acid phthalate as a primary standard.

The other method of obtaining a standard acid is to prepare a solution of the approximate strength desired and then standardize it by titration against some standard alkaline substance.

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[1] Kolthoff and Van Berk, J. Am. Chem. Soc. **48**, 2799 (1926).

[2] Hill and Smith, J. Am. Chem. Soc. **44**, 546 (1922).

Sodium carbonate is one of the most suitable of the alkaline substances and is best prepared by heating the pure bicarbonate to 270-300° C. or by fusing it in a platinum crucible in a current of dry carbon dioxide to prevent dissociation and the formation of sodium oxide, which renders the material hygroscopic.[1] Thallous carbonate, Tl_2CO_3, is also satisfactory. Sodium oxalate, which is used later for standardizing permanganate solutions, forms sodium carbonate when ignited, and may be used also for standardizing acids. Some acids may be standardized gravimetrically. For example, the chloride ion present in a definite volume of hydrochloric acid may be precipitated as silver chloride, from the weight of which the concentration of hydrochloric acid may be calculated. This is one of the most exact methods for standardizing hydrochloric acid, since the errors involved in titration are avoided.

Direct Preparation of Standard Hydrochloric Acid from the Constant Boiling Acid. Constant boiling hydrochloric acid of definite composition may be obtained by the method of Foulk and Hollingsworth.[2] In this process, concentrated hydrochloric acid is diluted to a density of about 1.1. The acid is placed in a flask and three-fourths of it is distilled off at the rate of 3-4 ml. per minute; the distillate is discarded. Most of the remainder is distilled at the same rate and collected. The reading of the barometer is recorded during the process. At a given barometric

TABLE XI. COMPOSITION OF CONSTANT-BOILING HYDROCHOLORIC ACID

Barometer, mm.	Per Cent HCl in Acid	Grams of Acid, Weighed in Air, Required for 1 Liter of 1.0 *N* Acid
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

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[1] Richards and Hoover, J. Am. Chem. Soc. **37**, 109 (1915).

[2] Foulk and Hollingsworth, J. Am. Chem. Soc. **45**, 1220 (1923). See also Hulett and Bonner, *ibid.*, **31**, 390 (1909), and Bonner and Branting, *ibid.*, **48**, 3093 (1926).

pressure, this last portion will always have the same composition. Table XI, p. 137, gives the data obtained by Foulk and Hollingsworth.

Procedure. Clean and dry one of the smallest glass stoppered conical flasks, and weigh it at room temperature. After weighing, do not touch the flask with the fingers or mark it in any way, but while holding it with a piece of paper or cloth run in as closely as possible the amount of constant boiling hydrochloric acid required for 1 liter of 0.1 N solution. Replace the stopper, taking care that none of the acid touches it, and weigh the flask and contents again immediately to avoid loss by evaporation or a change in weight of the flask from the condensation of moisture. Both weighings should be carried out within at least an hour of each other. In the meantime, have ready somewhat more than a liter of distilled water which has been aerated or boiled to expel carbon dioxide (this would act as an acid in certain cases), and then has been cooled. Immediately after the acid has been weighed, add to the flask an equal volume of water to prevent loss of acid; then transfer the contents carefully to a liter volumetric flask, washing out all the acid carefully with the boiled water. Dilute to the mark after the solution has attained room temperature, insert the stopper and mix the solution thoroughly by shaking and inverting the flask repeatedly. Transfer the acid to a suitable clean, dry bottle; stopper, and label it with the date of preparation and the normality of the solution. The weight of acid will probably be found to be slightly greater or less than the theoretical amount. It is necessary, therefore, to calculate the normality from the weight of the acid.

Calculation of Normality. The normality is the ratio of the weight of solute in a given volume of a solution to the weight of solute in the same volume of a normal solution. If the solution contains half of a gram-equivalent weight of solute per liter, it is half normal ($N/2$ or 0.5 N). From the last column of Table XI, p. 137, can be found the weight (in air against brass weights) of constant boiling acid which is required to make a liter of normal hydrochloric acid. The amount of acid in the sample actually weighed and diluted to a liter, divided by the weight needed for the same volume of normal solution gives the normality of the acid. *Example:* If the constant boiling acid was prepared at 750 mm. pressure, 179.979 g. would be required for a liter of normal acid. Suppose that a sample weighing 18.0500 g. was diluted to one liter. Then the normality of the resulting solution would be: $\frac{18.0500}{179.979} = 0.1003$.

A method often used involves the term "correction factor," which is the factor by which a certain volume of a particular standard solution must be multiplied to make it equivalent to that of a solution of some exact normality, as 0.5 N, 0.1 N, etc. Cor. Fact. = $\frac{\text{theoretical volume}}{\text{actual volume}}$, or $\frac{\text{actual weight}}{\text{theoretical weight}}$ for the same volume. In the foregoing example, the theoretical volume to which 18.0500 g. of constant boiling hydrochloric acid must be diluted to make the solution exactly 0.1 N is 1003 ml. The actual volume to which it was diluted was 1000 ml. Therefore the correction factor is 1.003. It is simpler, however, to calculate the normality. The use of normalities of solutions in calculating percentages will be taken up later.

Preparation of Standard Hydrochloric Acid by Standardization against Sodium Carbonate. *Procedure.* Directions for preparing 0.5 N hydrochloric acid will be given. From the data on the stock bottle of concentrated hydrochloric acid, calculate the volume of the acid which should be diluted to 2 liters to make 0.5 N acid. Measure this calculated volume of acid into a liter volumetric flask, add water, allow the solution to come to room temperature, dilute to the calibration mark, shake thoroughly, and pour the solution into a clean 2½ liter bottle. Fill the liter flask with distilled water to the mark, and add this to the acid solution. Shake the solution until it is uniform.

Prepare pure sodium carbonate from sodium bicarbonate.[1] A weighed platinum crucible, or a large glass-stoppered weighing bottle, previously weighed, is filled about three-fourths full of sodium bicarbonate (about 10 g.) and reweighed. The vessel is heated for 45 to 60 minutes at 270-300° C. It may be supported in a clean sand-bath, previously heated to drive out volatile organic matter from the sand, or in an asbestos ring within a large crucible, with the thermometer bulb close beside it at the level of the bicarbonate. After heating, cool the crucible or bottle in a desiccator for 40 minutes, and then weigh. Place

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[1] Lindner and Figala, Z. anal. Chem. **91**, 105 (1933); Smith and Croad; Ind. Eng. Chem. Anal. Ed. **9**, 141 (1937).

the vessel on a clean piece of black glazed paper, stir the contents with a glass rod, and brush particles that adhere to the rod back into the crucible or bottle. Heat as before for 30 to 45 minutes, cool and re-weigh. When the weight is practically constant, calculate the percentage of residue, which should be very close to the theoretical percentage. (Report, along with the standardization data.) Keep the pure sodium carbonate in a stoppered bottle in a desiccator until needed. Weigh from the weighing bottle into marked 250 ml. conical flasks two or more one-gram samples of the sodium carbonate, dissolve in about 75 ml. of water and titrate with hydrochloric acid as directed under "Determination of Sodium Oxide in Sodium Carbonate," p. 154, using the procedure employing either methyl orange or bromphenol blue as indicator. From the volume of acid required for each sample, calculate the normality of the acid. The calculation is not so simple as in the case already considered where the direct method was used in preparing the acid. The subject will therefore be taken up in detail.

Calculation of Normality. It is best to derive the normality entirely in terms of the primary standard substance, in this case, sodium carbonate. The weight of the primary standard divided by the number of ml. of solution to which it is equivalent, as found by titration, gives the weight of primary standard per ml. of titrating solution. Thus, if 1.0500 g. of sodium carbonate is required for the neutralization of 40.00 ml. of hydrochloric acid, 1 ml. of the acid would be equivalent to $\frac{1.0500}{40.00} = 0.02625$ g. of sodium carbonate. The equivalent weight of sodium carbonate is one-half the molecular weight, or 53.00. Therefore, the milliequivalent (abbreviation, m.e.) or the weight in 1 ml. of normal solution is 0.05300 g. The normality of the acid is obtained by dividing the weight of sodium carbonate corresponding to 1 ml. of the acid by the milliequivalent: $\frac{0.02625}{0.05300} = 0.4953\ N$. Note that the reasoning has been carried out entirely in terms of a solution of sodium carbonate that would be exactly equivalent to the solution of hydrochloric acid. It would, of course, be possible to calculate the weight of hydrochloric acid equivalent to 1.0500 g. of sodium carbonate and then to calculate the normality in terms of hydrogen chloride. This method is longer and more likely to result in errors of calculation. Still another method is to find the volume of normal solution to which 1.0500 g. of sodium carbonate is equivalent. This volume divided by 40.00 gives the normality.

Volumes and Normalities of Equivalent Portions of Two Solutions. In determinations of moderate exactness it is not necessary to standardize every solution against an appropriate primary standard, for a number of solutions may be standardized with the aid of one that has been standardized. If a volume V_1 of a solution of normality N_1 has been found to react exactly with a volume V_2 of a solution of unknown normality N_2, then $V_1 \times N_1$ = number of milliequivalents of the first substance, and $V_2 \times N_2$ = number of milliequivalents of the second substance; but the two volumes are equivalent, and each must represent the same number of milliequivalents. Hence $V_1 \times N_1 = V_2 \times N_2$.

Illustration: Fifty ml. of exactly 0.0500 N oxalic acid was neutralized by 24.95 ml. of sodium hydroxide solution. Find the normality of the latter:

$$50.00 \times 0.05000 = N_2 \times 24.95; \; N_2 = 0.1002$$

PREPARATION OF A STANDARD ALKALI

The hydroxides of sodium, potassium and barium are used for this purpose, since they are strong bases, and sufficiently soluble. None of these hydroxides can be obtained pure, a certain amount of water and alkali carbonates always being present, and they are very hygroscopic, especially the first two. It is therefore necessary to prepare a solution of approximately the proper concentration and then to standardize this alkali against hydrochloric acid of known normality, or against any of the primary standards just mentioned, as, for example, potassium acid phthalate.

Removal of the Carbonate from a Hydroxide Solution. When using certain indicators, exact results cannot be obtained with an alkali containing the carbonate ion which is always present. It may be removed in either of the following ways: 1. Sodium carbonate is almost insoluble in a saturated solution of sodium hydroxide and can be removed by decantation or filtration; 2. The carbonate ion is removed by precipitation as barium or strontium carbonate. The second method is slightly more practical and will be used here.

Procedure. For 1 liter of 0.1 *N* sodium hydroxide solution, weigh out on a platform balance about 7 g. of the crystals or 5 g. of the dry sticks or pellets of sodium hydroxide (what is the theoretrical weight?), place in a 400 ml. beaker and dissolve in 300 ml. of water. For a 0.5 *N* solution use five times as much alkali. Heat, and add slowly 20 ml. of 0.5 *N* barium chloride. Let the barium carbonate settle, and decant the clear solution into a 1000 ml. cylinder or marked bottle; dilute to 1000 ml. with water free from carbon dioxide. Let settle again and siphon or filter off the clear solution into a suitable bottle provided with a two-hole stopper. Through one hole, the end of a soda-lime tube is inserted to prevent the access of carbon dioxide, and through the other, a siphon tube provided at the lower end with a short rubber tube and pinch cock. By siphoning, the clear solution can be run into the buret without disturbing the precipitate. Contamination of the solution with carbon dioxide is thus avoided.

Standardization of 0.1 *N* Sodium Hydroxide. *Procedure.* Clean the burets thoroughly, drain out all excess of water and rinse each buret three times with a few ml. of the solution with which it is to be filled. Fill one with the 0.1 *N* hydrochloric acid prepared from the constant boiling acid and the other with the sodium hydroxide to be standardized. Read carefully the level of the liquid in each buret. Draw off into a 250 ml. conical flask approximately 40 ml. of 0.1 *N* hydrochloric acid, emptying the buret not faster than 0.7 ml. per second. Add three or four drops of methyl red solution, run in sodium hydroxide until the indicator just turns yellow, and take the reading on both burets, thus obtaining the number of ml. of sodium hydroxide equivalent to a definite volume of the acid. Phenolphthalein is almost as satisfactory if the solution is titrated to a *very faint* pink. The flask should be placed on a white background. While running in a solution from a burette, the flask must be constantly rotated with one hand, while the other hand-operates the stopcock. It requires some practice to attain the manual dexterity necessary to give the solution a smooth rotary motion instead of slopping it around as the beginner invariably does. When phenolphthalein is used the pink color will soon fade, due to the absorption of carbon dioxide from the air, but it should persist for at least 10-15 seconds. On this account the sodium hydroxide should never be run into the flask first and titrated with acid. (Would this trouble be experienced if methyl orange were used? Explain.) The end-point must be approached gradually, drop by drop; a little experience will soon enable one to judge when it is approaching. Try not to overstep it. If, however, this is done and too deep a color results, reverse the action by running in acid slowly until the end-point is reached, and then read both burets. It is possible in this way to titrate back and forth until a satisfactory end-point is obtained; such a titration cannot be as exact as one in which the end-point was not originally overstepped, on account of the absorption of carbon dioxide. A good rule to follow in all titrations is to take the buret reading when the end-point appears to have been reached, but is perhaps doubtful; then add another drop. If this oversteps the end-point, the previous reading was correct; if not, discard that reading, take a new one and then add another drop as before. The drop on the tip of the buret must always be removed by touching the tip to the side of the flask and then rinsing any liquid into the main solution with a spray from the wash bottle. Be sure that the stopcock does not leak and that the glass stopper does not loosen and allow the solution to run out.

Having obtained a satisfactory end-point, note carefully the total number of ml. of hydrochloric acid and of sodium hydroxide used. Then repeat the titration as before. The first titration will probably be somewhat inaccurate, but it will serve to indicate the approximate amount of sodium hydroxide required in the second; thus the end-point can be approached more quickly and also more carefully. In this second titration, however, it ought to be possible not to overstep the end-point. The two titrations may not agree within 0.2 ml. In such a case, run a third. If the volumes of sodium hydroxide required for duplicate samples of the same size are within 0.1 ml. of each other, these titrations may be considered satisfactory; otherwise another should be made. It is advisable to use at least 40 ml. of solution in a titration to avoid too large a percentage error. Thus, 0.1 ml. in 40 ml. is an error of 2.5 parts per thousand; if only 20 ml. was used, the error would be 5 parts per thousand.

When constant boiling hydrochloric acid is not available, potassium acid phthalate, reagent quality, is recommended. Dry it at 110° C., weigh out samples of approximately 0.9 g., dissolve in 50 ml. of water free from carbon dioxide and titrate with 0.1 N sodium hydroxide, using phenolphthalein as indicator. This is the titration of a weak acid and methyl red would, therefore, be unsuitable.

Solutions of alkalis should never be left in glass-stoppered burets over night.

Calculation of Normality. The number of ml. of acid multiplied by the normality gives the equivalent number of ml. of normal acid. Since this product is also equivalent to the number of ml. of alkali used in the standardization, the normality of the latter is: $\frac{\text{ml. of normal acid}}{\text{ml. of alkali used}}$. Thus, if 40.00 ml. of 0.1050 N acid required 45.00 ml. of alkali, the normality of the latter is $\frac{40.00 \times 0.1050}{45.00} = 0.0933$. Take the average of the figures obtained, which should agree within 0.0002. Do not calculate beyond the fourth significant figure. If the alkali has stood for a week or two, it should be restandardized. All the data must be entered in the notebook.

DETERMINATION OF REPLACEABLE HYDROGEN IN AN ACID

Principle. In this experiment, solid acids or acid salts are the unknowns to be analyzed. Since the particular acid present in the sample is not known, only the percentage of replaceable hydrogen which is common to all acids is determined. The sample is dissolved in water, free from carbon dioxide, and titrated with 0.1 N sodium hydroxide which is free from any carbonate. Phenolphthalein is used as indicator, since most of the acids are weak.

It is often desirable to titrate an aliquot part of a larger sample instead of the entire sample. Such a method is obviously less exact than that of titrating the entire sample, since the errors resulting from measuring out portions are involved. But it allows the solutions to be titrated back and forth in case the end-point is overstepped, an advantage in the hands of the student.

This method does not distinguish between different acids, but determines only the total replaceable hydrogen present, regardless of its source. If two acids are present and one of them can be determined by other means,—gravimetrically for example, as with hydrochloric acid and sulfuric acid,—then the weight of the second can be determined by calculating the difference if the sum of both is found by titration with an alkali. Before this subtraction can be performed, the results must be converted into the same molecular unit, e.g., ml. of normal solution, or weight of replaceable hydrogen.

Errors. Certain errors are common to all volumetric analyses: those due to change in temperature of solutions, to the measuring apparatus, and to the end-point. The end-point error, however, may be reduced by using larger samples. In this particular titration the presence of carbon dioxide in the air and in the solution tends to give high results, since this substance is acid towards phenolphthalein. The presence of a carbonate in the standard alkali has a similar effect.

Procedure. Weigh into 250 ml. conical flasks three samples of suitable size (see instructor), and dissolve in 50 ml. of water free from carbon dioxide (why?). The samples should be weighed out beforehand, so that one may proceed *at the beginning of the laboratory period* with the actual titrations.

Fill one buret with standard hydrochloric acid and the other with sodium hydroxide. Standardize the latter as previously directed. To the acid samples, add 2 or 3 drops of phenolphthalein, and run in sodium hydroxide until a faint pink is visible for 10-15 seconds, following the method used in standardizing the sodium hydroxide solution. It is important not to overstep the end-point, but, if this is done, titrate back the excess of alkali with the standard acid. If more than 50 ml. is required, the buret is simply refilled and the titration continued. If the results calculated to the same size of sample do not agree within 0.1 ml., titrate another sample. The percentage of replaceable hydrogen in the sample is taken as the average of the two results (or of three, if all are good). Remember that in all titrations it is always an advantage to know in advance approximately how much of the solution will be necessary. All of this work is done most conveniently in one laboratory period.

Instead of weighing out individual samples, a larger sample in a 250 ml. volumetric flask may be dissolved in water free from carbon dioxide, diluted to the mark and aliquot portions drawn off by a buret or a pipet.

For practice in the titration of a strong acid, weigh into small, weighed stoppered flasks or weighing bottles, samples of 0.15 to .20 g. (one or two drops) of reagent concentrated sulfuric acid, dilute with a little water and rinse into a 250 ml. conical flask with water free from carbon dioxide. Add a few drops of methyl red indicator and titrate with standard alkali as directed above. Instead of calculating replaceable hydrogen, the percentage of sulfuric acid should be calculated.

Calculation of Results. Since the volume of the standard solution used determines the weight of the substance sought, it is first necessary to know the weight of the latter equivalent to 1 ml. of a normal solution. This has been defined as the milliequivalent weight (abbreviation, m.e.). One liter of normal acid solution contains 1.008 g. of replaceable hydrogen, and 1 ml. contains 0.001008 g. The volume of the alkali used in the titration multiplied by its normality gives the corresponding volume of normal solution. This latter volume multiplied by the milliequivalent of hydrogen gives the weight of replaceable hydrogen in the sample. It remains now to divide the weight of substance sought by the weight of the sample—if the whole sample was titrated—and to multiply by 100 to obtain the percentage sought. In this case, the percentage will be very small on account of the low equivalent weight of hydrogen, and the value must be carried out to the fourth significant figure. An error of 0.002 per cent in this determination is, therefore, significant. Results should check within at least three parts per thousand.

If the sample was diluted to a definite volume and an aliquot part was taken for titration, the weight of the sample titrated is equal to:

$$\frac{\text{Wt. original sample} \times \text{ml. taken for titration}}{\text{ml. to which sample was diluted}}.$$

Illustration: A 2.500 g. sample of acid was diluted to 250.0 ml. and the 40.00 ml. of it taken for a titration required 48.00 ml. of 0.0980 N sodium hydroxide. This volume would be equivalent to $48.00 \times 0.0980 = 4.704$ ml. of normal alkali. Since the m.e. of hydrogen is 0.001008, the weight of hydrogen in the sample titrated would be $0.001008 \times 4.704 = 0.004742$ g. The weight of the sample titrated is $2.5 \times \frac{40.00}{250.0} = 0.4000$ g. Then $\frac{0.004742}{0.4000} \times 100 = 1.186$ per cent of hydrogen.

If it is desired to calculate the percentage of a known acid, for example, sulfuric acid, the m.e. of this acid (0.04904) is substituted for that of hydrogen.

In volumetric problems it is usually possible to calculate first the m.e. of the substance sought, and from this the weight of the substance sought, without solving a proportion as is often done in gravimetric analysis. Remember that the equivalent weight depends ultimately on the reaction that takes place with the standard solution. When using this method, *never calculate the weight of the reagent contained in the standard solution.* That was done when the solution was prepared. Henceforth, the concentration of the solution is expressed in terms of normality. For example, in calculating the weight of replaceable hydrogen in an acid, it is never necessary to use the weight of sodium hydroxide per ml. in the standard alkali, provided the normality is known.

If it is desired to use the correction factor method, the volume of standard solution used in the titration is multiplied by the correction factor to convert it into the equivalent volume of solution of some exact normality, for example, 0.1 N solution. The rest of the calculation differs only slightly from that given above.

The titer method should also be mentioned. The word *titer* refers to the strength of a solution as determined by titration. The titer of a solution is usually expressed in grams of substance per ml. It is possible to derive titers and solve problems without making use of the concepts of equivalent weight and normality.[1]

Illustration: The titer of a sodium chloride solution was found to be 0.005905 g. of sodium chloride per ml. In the titration of a 0.3698 g. sample of a silver alloy, 30.50 ml. of the sodium chloride solution was used; the percentage of silver is to be found. The weight of sodium chloride which is equivalent to the silver is T (titer) $\times$ V (volume), or 0.005905×30.50.

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[1] These and other advantages of the titer method are pointed out by W. P. Cortelyou, J. Chem. Ed. **9**, 1297 (1932).

The weight of silver may be derived by proportion:

$$\begin{array}{ccccccc} \text{Wt. NaCl} & : & \text{wt. silver} & :: & \text{mol. wt. of NaCl} & : & \text{At. wt. of Ag} \\ 0.005905 \times 30.50 & : & x & :: & 58.46 & : & 107.88 \end{array}$$

$$x = 0.3324 \text{ g. silver}$$

Then

$$0.3698 : 0.3324 :: 100 : \text{per cent of silver,}$$

or

$$\text{per cent of silver} = 89.87.$$

In this method, the weight, x, of substance found is equal to $T \times V \times \frac{107.88}{58.46}$. Note that the numerical ratio is an ordinary gravimetric factor (see Chap. XV, p. 306 ff). Tables of such factors are available. Hence the calculation of percentages by means of the titer may be made by the following general formula:

$$\text{Per cent of substance sought} = \frac{V \times T \times \text{factor}}{W} \times 100,$$

in which W stands for weight of sample, and the factor must be appropriate to the particular process in question.

REVIEW QUESTIONS AND PROBLEMS

1. In each of the following give (a) hypothetical or actual equation (b) class of reaction (c) equivalent of first substance (d) reason.

   1. UO_2Cl_2 to $(UO_2)_2Fe(CN)_6$ 3. $AsCl_3$ to NaCl and H_3AsO_3
   2. FeS to $FeCl_3 + H_2SO_4$ 4. HIO_3 to ICl

2. Fifty ml. of hydrochloric acid solution yields 0.8000 g. of silver chloride. Calculate the normality of the acid.

3. How many ml. of perchloric acid, $HClO_4$, specific gravity 1.207 and containing 30.00 per cent of perchloric acid, would be required for the preparation of 5.000 liters of 0.1000 N acid? Ans. 138.7 ml.

4. Five-tenths g. of sulfamic acid, HSO_3NH_2, requires 40.00 ml. of sodium hydroxide for neutralization. Calculate the normality of the alkali solution.

5. Reagent nitric acid has a density of 1.42 and contains 70.0 per cent of HNO_3. What is the normality of the acid?

6. The sulfur in 1.000 g. of steel is burned to sulfur trioxide, SO_3, and absorbed in 50.00 ml. of 0.0100 N alkali. The excess of hydroxide requires 24.00 ml. of 0.0150 N acid. What is the per cent of sulfur in the steel?

7. Calculate the pH of a solution obtained by adding 20 ml. of 0.5 M hydrochloric acid to 60 ml. of 0.5 M ammonium hydroxide.

8. Five g. of an aqueous solution containing both H_3PO_4 and KH_2PO_4 require 80.00 ml. of 0.1000 *N* alkali using phenolphthalein as indicator. Another 5.000 g. sample requires 30.00 ml. of the alkali using methyl orange as indicator. Calculate the percentage of H_3PO_4 and KH_2PO_4 present.

Ans. 5.88 per cent H_3PO_4. 5.45 per cent KH_2PO_4.

9. Explain how to determine volumetrically the percentage of each phosphate in a mixture containing Na_2HPO_4, Na_3PO_4 and inert substances.

10. Compare the titration of a weak acid at room temperature and at a temperature near the boiling point, and explain the difference.

11. A 0.3000 g. sample of sodium oxalate is heated to form carbonate, and the latter, when titrated using methyl orange indicator, requires 45.00 ml. of acid. Calculate the normality of the acid but do not calculate the weight of sodium carbonate.

12. It is desired to dilute a solution of hydrochloric acid of which 50.00 ml. yielded 0.8000 g. of silver chloride in order to make it exactly 0.1000 *N*. If 500 ml. of the acid is available, to what volume must it be diluted?

13. What is the normality of a solution of sodium hydroxide of which 50.00 ml. added to 0.6000 g. of sulfamic acid, HSO_3NH_2, required for back titration 10.00 ml. of standard acid, 1.00 ml. of which was equivalent to 0.005300 g. of sodium carbonate?

Ans. 0.1436 *N*.

14. A solution of sodium hydroxide contaminated with carbonate when standardized against hydrochloric acid using methyl orange as indicator is found to be 0.1100 *N*. When titrated, using phenolphthalein in the cold, it is calculated to be 0.1050 *N*. Calculate the gram equivalents of sodium hydroxide and of sodium carbonate per liter.

15. A solution of sulfur trioxide, SO_3, in sulfuric acid requires 70.00 ml. of 0.8000 *N* alkali for a sample weighing 2.600 g. What is the percentage of each constituent?

16. What volume of water must be added to 100 ml. of 0.1 *N* acetic acid to give a *p*H of 3?

17. A sample weighing 0.5000 g. requires 20.00 ml. of 0.1000 *N* acid when phenolphthalein in cold solution is used as indicator and 60.00 ml. of the acid when methyl orange is used. Which of the three alkaline substances, NaOH, Na_2CO_3 and $NaHCO_3$ are present and what percentage of each?

Ans. 42.40 per cent of Na_2CO_3 and 33.60 per cent of $NaHCO_3$.

18. Explain the titration of a salt of a very weak acid, including (a) several examples of this case (b) standard solution used (c) the approximate *p*H at the end-point for a particular example (d) the indicator used and why. Why is it impossible to titrate sodium acetate with hydrochloric acid?

19. One gram of a mixture containing only K_2CO_3 and Li_2CO_3 requires 195.1 ml. of 0.1000 *N* acid when titrated, using methyl orange as indicator. What per cent of each of the carbonates is present?

Suggestion: let x equal the weight of K_2CO_3, then $1 - x =$ weight of Li_2CO_3.

Ans. 60.00 per cent K_2CO_3, 40.00 per cent Li_2CO_3.

20. What weight of sample must be taken in order that with 0.1000 N acid, the number of ml. used will give the percentage of sodium oxide?

Ans. 0.3100 g.

DETERMINATION OF SODIUM OXIDE IN SODIUM CARBONATE

Principle. It has already been explained how it is possible to titrate a strong base combined with a very weak acid, provided the latter is so weak that its solution does not show an acidic reaction towards the indicator used. A saturated solution of carbon dioxide was shown to have a pH not far from 3.9, the value at which methyl orange and bromphenol blue change color. If the same principle is applied to the salt of an acid stronger than carbonic acid, such an acid would appreciably affect these indicators (even carbonic acid affects them slightly), and it would be necessary to find another indicator, the color change of which would occur at a lower pH. It would thus appear possible to titrate in the presence of acids stronger than carbonic acid, but, as has already been explained on pp. 117-123, at such a low pH, the end-point soon becomes so indistinct that the method is of no value. The weaker the acid present, the sharper the end-point. The strength of an acid is shown by its dissociation constant, that of the first hydrogen of carbonic acid being 3×10^{-7}. The titrating solution must be a strong acid such as hydrochloric acid. The student should be able to select from the list given in the Appendix four acids, other than carbonic acid, the alkali salts of which can be titrated by this method.

Samples of the carbonate are dissolved in water and titrated with hydrochloric acid:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2CO_3.$$

Carbonic acid decomposes largely into carbon dioxide and water. The end-point with methyl orange, which is neither yellow nor red but an intermediate reddish orange color, may be greatly improved by adding an inert blue dye, cyanole FF., as mentioned on p. 478. The addition of methylene blue to methyl red improves the color change.[1] The end-point with 0.1 N solutions

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[1] A. H. Johnson and J. R. Green, Ind. Eng. Chem. Anal. Ed. **2**, 2 (1930).

is not very sharp, for carbonic acid contains a concentration of hydrogen ion sufficient to give a solution of *p*H approximately 3.9. If the indicator is added to water and also to a solution of carbonic acid, the former will be yellow and the latter orange. In precise work, it is necessary to use as a standard for comparison a saturated solution of carbon dioxide containing the same concentration of indicator, and to carry out the titration to this same shade of color. Since this comparison solution is unstable, owing to loss of the gas, other standards have been proposed. A solution containing 0.2 g. of potassium biphthalate in 100 ml. of water has the same *p*H, and therefore gives the same color with the indicator as a titrated solution from which the carbon dioxide has not been removed. Such a solution is permanent. For the same reason a greenish blue color intermediate between blue and yellow shows the end-point with bromphenol blue. If the acid formed in the titration of the salt can be volatilized by boiling the solution, for example, carbonic acid, hydrocyanic acid, and hydrosulfuric acid,—other indicators, such as methyl red, may be used and a sharp end-point obtained by adding enough standard acid to cause a visible change in the indicator, boiling off the acid liberated, and finishing the titration as usual. The rate of change of color of the indicator (methyl red) at the end-point is about seven times as great as in the methyl orange method. The *p*H of this solution at the end-point is between 5 and 6. The small amount of very weak acid remaining has no appreciable effect on the indicator. The color change cannot be as readily distinguished by artificial light.

If the salt of a volatile acid, as carbonic or hydrochloric acid, is to be analyzed, an indirect method employing other indicators, as methyl red, bromthymol blue or phenolphthalein, may be used. First, an excess of standard acid is added; in the case of sodium carbonate this will be somewhat more than twice the amount required to decolorize phenolphthalein, the change with this indicator occurring when the carbonate is half neutralized to form bicarbonate ($NaHCO_3$). The carbonic acid is removed by long boiling, the solution then containing only sodium chloride and hydrochloric acid. The excess of acid is determined by titration with standard sodium hydroxide. The two methods should give identical results when methyl red is used, but with phenolphthalein the results are slightly low, owing to the difficulty of removing the last traces of carbon dioxide. Ammonium ion in salts is determined by adding an excess of sodium hydroxide, distilling off the ammonia into an excess of standard acid and titrating back with standard sodium hydroxide, using methyl red as indicator. (Why?)

Errors. Aside from the errors common to all volumetric processes, the chief source of error in this experiment is the indistinctness of the end-point. The presence of too much indicator makes this still worse. The solution may be boiled down too far in removing carbon dioxide, thus allowing some hydrochloric acid to escape, and causing high results, or it may not be boiled long enough to expel all the carbon dioxide present, thus causing low results. (Why?)

Other Applications. Consider the various salts that may be titrated in this way, including those of barium, strontium and calcium. If these salts are insoluble, they must be dissolved in an excess of acid and this excess titrated. Carbon dioxide is determined volumetrically by absorbing it in excess of standard barium hydroxide, and, without filtering off the barium carbonate, titrating the excess with standard acid, using phenolphthalein as indicator. A good end-point is obtained. Or the barium carbonate may be filtered off, dissolved in an excess of standard acid, and the excess titrated back.

For the determination of a carbonate and a hydroxide in the presence of each other, two methods are available.

Method 1. The carbonate is precipitated with barium chloride and, without filtering, the solution is titrated with standard acid, using phenolphthalein as indicator. A strontium salt is better that a barium salt because the carbonate becomes dense and crystalline more readily. The hydroxide is determined in this way. Another sample is titrated for both the hydroxide and the carbonate, using methyl orange or bromphenol blue as indicator. The difference between these two volumes of acid represents the volume required for the carbonate, which has an equivalent of one-half its molecular weight. This method is more satisfactory than the following one.

Method 2. Using phenolphthalein as indicator, the cold solution is titrated with acid which neutralizes the hydroxide and forms bicarbonate from the sodium carbonate. The titration is continued with methyl orange or bromphenol blue as indicator, and the bicarbonate is converted into a neutral salt such as sodium chloride. In this latter reaction, the equivalent of sodium carbonate is the molecular weight, and the amount is readily calculated. If the volume of acid used in the second titration is subtracted from that used in the first, the difference is the volume required for the hydroxide. (Why?) The end-point is not very sharp when a carbonate is titrated to a bicarbonate, so that in practice other methods are preferable.

For the determination of a carbonate and a bicarbonate in the presence of each other, two methods are available.

Method 1. $NaHCO_3 + NaOH = Na_2CO_3 + H_2O$. Because there is no way of carrying out this titration directly, an excess of standard alkali is added; sodium carbonate is not affected. Barium chloride or a strontium salt is then added to precipitate all the carbonate. Without filtering, the excess of sodium hydroxide is titrated with standard acid, with phenolphthalein as indicator. Since the equivalent of sodium bicarbonate is the molecular weight, the volume of sodium hydroxide used in converting it to a normal carbonate determines the weight of sodium bicarbonate present.

A new sample of the same size is titrated with acid, with methyl orange or bromphenol blue as indicator. The bicarbonate requires a volume of acid equal to the volume of sodium hydroxide required in the above reaction if these solutions are of the same normality. If, therefore, this latter volume is subtracted from the total volume of acid required, the difference is the volume used to neutralize the carbonate, thus:

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2,$$

from which the weight of sodium carbonate can be readily calculated. This is the most satisfactory method of determining the carbonate and the bicarbonate in a sample.

Method 2. If phenolphthalein is used as indicator in a cold solution, the following reaction occurs:

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

The bicarbonate already present is unaffected. This titration determines the amount of carbonate, the equivalent of which in this reaction is the molecular weight. Since, at this point, the phenolphthalein has become colorless, methyl orange or bromphenol blue should be added and the titration continued:

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

This bicarbonate is a mixture of the bicarbonate originally present and that formed in the preceding titration. The latter will require the same volume of acid as was used in the first titration. If, therefore, this volume is subtracted from the volume used in the second titration, the difference is the volume required for the bicarbonate originally present, the equivalent being the molecular weight. Or, a separate sample of the same size may be titrated, with methyl orange as indicator. In this case, if the volume of acid is x ml., then the volume for the bicarbonate originally present is $x - 2y$, instead of y ml., as when the same sample is used.

Procedure for Sodium Oxide in Sodium Carbonate. Methyl Orange or Bromphenol Blue Method. Weigh two samples of about 0.3 g. each into 250 ml. conical flasks, dissolve in 50 ml. of water and add a few drops of methyl orange or bromphenol blue, or enough to give the solution a light yellow or blue color according to the indicator used. (Avoid using too much indicator.) To a similar flask add 100 ml. of a solution containing 2.0 g. of potassium biphthalate, $KHC_8H_4O_4$, per liter and add the same amount of indicator. This will give an orange or purplish green color half way between yellow and pink or blue and green. If the modified methyl orange is used, the color should be almost a gray, midway between green and magenta. Fill one buret with standard alkali and the other with 0.1 N hydrochloric acid. Run in hydrochloric acid until the color exactly matches that of the phthalate buffer, the pH of which is close to 4. (See p. 150.) The colors cannot be accurately matched by ordinary artificial light, and therefore this titration should be carried out by daylight. Changes in color of methyl orange are most distinct when viewed by the light of the General Electric Daylight fluorescent lamp, perhaps due to a very slight excess of blue. This has been found to be superior to daylight. If the end-point is overstepped, titrate back with standard alkali. Remember what was said on page 143 about finding the proper reading at the end-point. Titrate another sample of the carbonate, and if the results calculated to the same size of sample do not agree within 0.1 ml., run a third titration.

If preferred, a 1.5 g. sample may be weighed into a 250 ml. volumetric flask, the solution diluted to the mark and aliquot portions taken with a pipet for titration.

Calculation of Results. The volume of hydrochloric acid is multiplied by its normality to convert it into ml. of normal acid. According to the equation, one mole of sodium carbonate reacts with two moles of hydrochloric acid; therefore, the equivalent of sodium carbonate is $\frac{Na_2CO_3}{2}$, and that of sodium oxide is $\frac{Na_2O}{2}$, or 31.00 g. Its milliequivalent is, therefore, 0.03100 g. By multiplying the number of ml. of normal acid used by the m.e., the weight of sodium oxide in the sample titrated is found. The weight of the sample titrated and the percentage of sodium oxide are obtained in the manner described on p. 147. Duplicates should check within two parts per thousand. The average of the results on samples 1 and 2 is accepted as the most probable value for those samples. To illustrate the calculation, an example is given:

Wt. sample + bottle	9.7320
Wt. bottle	9.4248
Wt. sample 1	0.3072

This required 40.20 ml. of 0.1050 N HCl.

$$1 \text{ ml. } N \text{ HCl} = 0.03100 \text{ g. } Na_2O$$

$$40.20 \times 0.1050 = 4.221 \text{ ml. } N \text{ HCl}$$

$$4.221 \times 0.031 = 0.1309 \text{ g. } Na_2O$$

$$\frac{0.1309}{0.3072} \times 100 = 42.61 \text{ per cent of sodium oxide.}$$

Procedure. Methyl Red Method. (a) This method is excellent if 0.1 N acid is used, but it is not satisfactory with 0.5 N acid. Add to each sample two or three drops of methyl red. Run in a standard acid until the solution has changed from a yellow to a pink coloration. Add two drops of acid in excess. This is just insufficient to react with all the carbonate. A large excess is undesirable, because it would necessitate back titration with alkali. Place the flask over a flame which will bring the solution to the boiling point in two minutes, and boil for two or three minutes, or until the solution has changed from red back to yellow, due to the removal of carbon dioxide. Wash down the sides of the flask with distilled water, cool, and continue the titration with standard acid until the red coloration just reappears. This is the proper end-point. Calculate the results. Be careful not to overstep the end-point, but, if this occurs, titrate back with standard alkali and approach the end-point again with the acid. The trace of carbon dioxide which remains has no effect on the indicator.

The results are calculated as in the preceding determination where methyl orange was used as an indicator.

Method (b). A somewhat more accurate method consists in adding an excess of acid, boiling off all the carbon dioxide and titrating back with standard alkali.

Add to each sample in a 500 ml. flask two or three drops of methyl red and run in standard hydrochloric acid until the color changes, then about 1 ml. more to be sure of a slight excess. A large excess is undesirable, for the possibility of loss of hydrochloric acid in the subsequent evaporation is greater. Boil down to 40 ml. (not too far, or hydrochloric acid will be volatilized), taking care that no loss occurs by spattering or bumping. Four or five glass beads will often prevent the latter. All carbon dioxide is not easily removed, and although no attempt was made to remove it in the methyl orange method, this is necessary here. (What effect would its presence have on results?)

Cool the samples and titrate with sodium hydroxide until the color just changes to orange or yellow. Be careful not to overstep the end-point, but if this occurs, titrate back with hydrochloric acid just as in standardizing the alkali.

If phenolphthalein is used instead of methyl red, the results are somewhat less accurate because the last traces of carbon dioxide are difficult to remove and the pH of the solution does not reach the value of 8 or 9 at which this indicator becomes pink unless a slight excess of hydroxide is added.

In calculating results, convert the number of ml. of sodium hydroxide used into ml. of N sodium hydroxide by multiplying by its normality. Do the same with the hydrochloric acid. The difference between the volumes of normal acid and alkali used is the volume of normal acid required to react with the sodium carbonate. This is what would have been required if the carbonate had been titrated directly, using methyl orange or bromphenol blue; the rest of the calculation is the same as described there. With careful work the results of both methods should agree within about three parts per thousand. Report each method separately, but on the same report blank.

THE KJELDAHL METHOD FOR THE DETERMINATION OF NITROGEN IN ORGANIC COMPOUNDS

An important method of determining nitrogen in organic compounds is that devised by Kjeldahl in which the organic matter is oxidized to carbon dioxide and water by boiling with concentrated sulfuric acid, the latter being reduced to sulfur dioxide. The nitrogen is thus converted into ammonium sulfate, unless it was originally present as azo or nitro derivatives. In this case it is first treated with a mixture of salicylic acid and sulfuric acid and the nitrated derivative thus formed is reduced with thiosulfate to an amino derivative. After the organic matter has been destroyed, an excess of sodium hydroxide is added to the sulfuric acid and the liberated ammonia is distilled into a measured volume of standard acid. The excess of the latter is then titrated with standard alkali, using methyl red as indicator.

Many modifications of the Kjeldahl method have been suggested for the purpose of accelerating the process of digestion with sulfuric acid. The catalysts proposed for this purpose include mercury, copper and selenium or combinations of these. In the Gunning modification no catalyst is employed but the boiling point is raised by the addition of potassium or sodium sulfate, thus permitting the use of a higher temperature. If mercury or copper is used, it must be precipitated by adding sodium sulfide to the alkaline solution before distilling off the ammonia.

Procedure. Weigh out three 1 g. samples, wrap each of them in a 9 cm. filter paper and drop it into a dry 500 ml. Kjeldahl flask. The paper wrapper prevents any of the material from clinging to the neck of the flask and thereby escaping digestion.

Add 0.1 g. of selenium and 10 g. of potassium or sodium sulfate (the latter must be anhydrous). Pour 25 ml. of conc. sulfuric acid carefully into the flask. Place the flask in an inclined position at an angle of 30°-45° in a hood or preferably in a digestion rack where provision is made for the removal of sulfuric acid fumes. Heat the mixture in the flask gradually until the sulfuric acid boils gently. If desired, the portion of the flask above the acid may be protected from the flame by a square of asbestos in which is a hole of the proper diameter. Considerable frothing and foaming may occur during the first few minutes of heating and the flask should be watched closely during this period to prevent any portion of the sample from being carried into the neck of the flask. If the foaming is very bad, add a small piece of paraffin. Continue to boil the mixture gently until the liquid has become colorless or a light yellow and no undissolved particles are present, showing that all carbon has been oxidized. This will require from 30 minutes to 2 hours, depending on the nature of the sample. When the digestion has been completed, remove the flame and allow the flask to cool, shaking it occasionally as it begins to solidify.

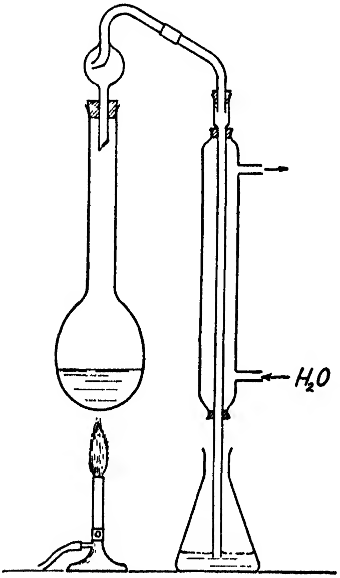

Fig. 41. Distillation of Ammonia After a Kjeldahl Digestion. The long-necked digestion flask is connected to the condenser by means of a special trap to prevent the strongly alkaline mixture in the digestion flask from being carried over mechanically.

Good results are obtained by using either the alkali sulfate or the selenium but the time is shortened if both are used. Instead of selenium, 0.2 to 0.3 g. of selenium oxychloride may be added to the sulfuric acid before the latter is poured into the flask.

Some selenium is volatilized and condenses as a red deposit in the neck of the flask.

To the *thoroughly cool* acid add carefully, a little at a time with frequent shaking, 100 ml. of water, cooling the flask under the tap. Prepare for each sample a solution of 45 g. of stick sodium hydroxide in 75-100 ml. of water and cool it. If preferred, a stock solution of 35 per cent sodium hydroxide may be made up and 100 ml. of this used for each sample.

Set up a distillation apparatus as shown in Fig. 41. The bulb between the flask and condenser is called a Kjeldahl trap and its purpose is to prevent any of the alkaline solution from being carried as a spray into the condenser. The lower end of the condenser is fitted with a rubber stopper to which is attached a bent adapter which extends nearly to the bottom of a 500 ml. conical flask. Clamp the digestion flask, condenser and receiver into position.

Remove the receiver and measure into it accurately from a pipet or buret, 50 ml. of standard 0.1 *N* hydrochloric or sulfuric acid. Add three drops of methyl red indicator. Replace the flask, taking care that the tip of the adapter reaches below the surface of the acid. Disconnect the digestion flask, and holding it in a slanting position, carefully pour down the side, so as to form two liquid layers, the solution of sodium hydroxide described above. Drop a piece of litmus paper and a few pieces of mossy zinc into the flask, the purpose of the latter being to prevent bumping during the distillation by furnishing a stream of hydrogen bubbles. Connect the flask to the trap and condenser and mix the two layers of acid and alkali by swirling gently, being careful that they do not mix suddenly. The solution must be alkaline as shown by the strip of litmus paper. If it is not, more sodium hydroxide must be added.

Heat the solution to boiling and distill rapidly about half the solution. The process must be constantly watched in order to prevent temperature fluctuations which might cause acid from the receiver to be drawn back into the Kjeldahl flask. Steam distillation is sometimes used here. If the solution in the receiver should become alkaline as indicated by the color of the methyl red indicator, add more standard acid. Disconnect the Kjeldahl flask to prevent acid from being sucked back, *then* remove the flame and rinse out the condenser and adapter with water, allowing the washings to run into the receiver. Titrate the excess of standard acid with standard alkali. Standardize the latter by titrating a measured volume of the acid.

It is advisable to rinse out the Kjeldahl flask while it is still hot.

A blank should be run on the reagents and care taken that no ammonia is absorbed from the atmosphere during the analysis.

Calculation. Multiply the volume of each standard solution by its normality and subtract these volumes of normal solution to find the ml. of normal acid required to neutralize the ammonia. Multiply this by the m.e. of nitrogen, which is 0.01401 and calculate the per cent of nitrogen in the sample.

Review Questions and Problems

1. A sample of nitrogenous material weighing 1.0580 g. is decomposed by the Kjeldahl method. The ammonia is distilled into 50.00 ml. of 0.1060 *N* acid and 10.10 ml. of 0.0980 *N* alkali is required to titrate the excess. What per cent of nitrogen in the sample?

2. Fifty ml. of hydrochloric acid after precipitation by excess of silver nitrate yields 0.8060 g. of silver chloride. Calculate the normality of the acid.

3. One g. of pure potassium bitartrate, $KHC_4H_4O_6$, is ignited to potassium carbonate and titrated with acid, of which 45.55 ml. was required, using methyl orange. Calculate the normality of the acid.

Note. Do not calculate the weight of carbonate, but find the equivalent of the tartrate from the number of equivalents of potassium carbonate that can be formed from it.

4. In problem 3, how much 0.1150 *N* alkali would be required to titrate the bitartrate? How does its equivalent in this problem compare with its equivalent in problem 3?

5. A sample weighing 0.5015 g. contains sodium hydroxide, sodium carbonate and inert material. When titrated with 0.2200 *N* acid after adding excess of barium chloride and using phenolphthalein as indicator, 40.10 ml. is required. Another sample of the same size, using bromphenol blue as indicator requires 50.50 ml. Calculate the percentages of sodium hydroxide and sodium carbonate in the mixture.

Ans. 70.36 per cent NaOH; 24.18 per cent Na_2CO_3.

6. A sample weighing 0.6020 g. contains sodium carbonate and bicarbonate and inert material. It is titrated in the cold with 0.1060 *N* acid, using phenolphthalein as indicator, and requires 40.20 ml. Another sample of the same weight, using bromphenol blue as indicator, requires 95.40 ml. Calculate the percentage of sodium carbonate and sodium bicarbonate in the mixture.

Ans. 75.02 per cent Na_2CO_3; 22.19 per cent $NaHCO_3$.

7. A sample weighing 0.4850 g. contains sodium carbonate and bicarbonate. To it is added 40.00 ml. of 0.1000 *N* sodium hydroxide and an

excess of barium chloride. The excess of alkali requires 10.00 ml. of 0.1000 *N* acid, using phenolphthalein as indicator. Another sample of the same weight requires 70.00 ml. of 0.1000 *N* acid, using bromphenol blue as indicator. Calculate the percentage of sodium carbonate and sodium bicarbonate in the sample.

8. Draw titration curves for phosphoric acid and for sodium carbonate.

9. Calculate *p*H at the end-point in the titration of 0.10 *N* sodium borate with 0.10 *N* hydrochloric acid, considering boric acid as HBO_2. What indicator would be suitable and would the end-point be sharp?
Ans. *p*H is 5.26.

10. If the error in reading a buret is 0.02 ml., what is the total error from this source in parts per thousand when 25 ml. of solution is used? When 40 ml. is used? When 60 ml. is used (the buret being refilled)?

11. One hundred ml. of hydrochloric acid, treated with excess of calcium carbonate, liberates 0.2500 g. of carbon dioxide. What is the normality of the acid?

12. A solution contains only hydrochloric and phosphoric acids. Explain how to determine the amount of each one by titration with alkali only.

13. One g. of crude sodium nitrate is reduced to ammonia, which is distilled into 90.10 ml. of 0.1250 *N* acid. The excess requires 5.05 ml. of 0.1200 *N* alkali. What is the per cent of sodium nitrate in the sample?

14. A certain weight of Na_2S_x requires 15.00 ml. of normal acid to titrate the sodium present and 45.00 ml. of normal alkali to unite with the sulfate formed, when excess of hydrogen peroxide is added to the alkali solution, thus: $Na_2S_x + (3x + 1)H_2O_2 + (2x - 2)NaOH = xNa_2SO_4 + 4xH_2O$. What is the value of x in the formula?
Ans. 4.

15. Describe four methods of obtaining standard hydrochloric acid.

CHAPTER IX

VOLUMETRIC PRECIPITATIONS. COMPLEX FORMATION

THEORY AND PROCEDURES

The application of precipitation reactions to analytical purposes is in certain respects a simpler matter in the volumetric branch than in the gravimetric. In the latter the separation of the precipitate from many or all of the other substances in the solution is essential, whereas in a titration it is a matter of indifference if the precipitate carries down with it adsorbed material, provided the reagent and the substance to be titrated react stoichiometrically. Further details regarding gravimetric precipitations and separations by precipitation are to be found in Chapters XV, XVI and XVII. The theory of precipitation and of complex-formation rests upon the principles of chemical equilibrium as applied in these cases; calculations based upon complex-dissociation constants and upon solubility-product constants are essential.

The Solubility Product Principle. In the saturated solution of a difficultly soluble electrolyte the product of the molecular concentrations of the ions, each raised to the power corresponding to the coefficient of that ion in the balanced ionic equation for the precipitation, is a constant at constant temperature. This is the solubility product principle.

Illustrations:	*Solubility product expression:*
Reaction:	
$Ag^+ + Cl^- = \downarrow AgCl$	$[Ag^+]\ [Cl^-] = S_{AgCl}$
$2Ag^+ + CrO_4^{=} = \downarrow Ag_2CrO_4$	$[Ag^+]^2\ [CrO_4^{=}] = S_{Ag_2CrO_4}$
$Ce^{+++} + 3F^- = \downarrow CeF_3$	$[Ce^{+++}]\ [F^-]^3 = S_{CeF_3}$

The letter *S* is used to denote the solubility product constant, and the formula written as a subscript to the *S* indicates the salt to which the constant applies. Table XXII in the Appendix gives the numerical values of the constants for many substances that are used in analysis.

In volumetric analysis the sharpness of the titration depends upon the amounts of the ions of the precipitate that remain in solution at the equivalence-point, and upon the effect of a slight excess of the reagent upon the solubility of the substance that is being precipitated. In the case of the formation of a soluble complex salt, similar considerations apply, except that a complex-dissociation constant is used rather than a solubility product constant in considering the theoretical possibilities of a process.

Illustration: At the equivalence-point of the titration of silver with thiocyanate the solution is saturated with silver thiocyanate. At this point how much silver in grams per 100 ml. of solution remains unprecipitated? The solubility product of silver thiocyanate is $10^{-12} = S_{AgCNS}$ (Table XXII, App.). The problem reduces to finding the weight of silver in 100 ml. of saturated silver thiocyanate, except that at the end of a titration there are present potassium nitrate, nitric acid and ferric nitrate, the latter to indicate excess of thiocyanate ions; these foreign substances increase the solubility of the silver thiocyanate slightly, but this effect will be neglected here. In the saturated solution $[Ag^+] = [CNS^-]$ since equivalent amounts of the two ions have been brought together. Hence $[Ag^+] = [CNS^-] = \sqrt{10^{-12}} = 10^{-6}$ molar. One mole of silver ion weighs 107.88 g. and hence there is 107.88×10^{-6} g. of silver per liter, or 107.88×10^{-7} g. per 100 ml., or 0.0000108 g. or, rounded, 0.01 mg. per 100 ml. As soon as a slight excess of the thiocyanate ion is present, the solubility of the silver thiocyanate is still smaller. If one drop, i.e., 0.05 ml. of 0.1 *N* thiocyanate is present per 100 ml. the concentration of the thiocyanate ion is $\frac{0.05 \times 0.1}{100} = 5 \times 10^{-5}$ molar (since the equivalent weight and the molecular weight are identical for CNS^-). Upon substituting this value into the solubility product expression, $[Ag^+][CNS^-] = 10^{-12}$, the concentration of silver ion is: $[Ag^+] = \frac{10^{-12}}{5 \times 10^{-5}} = 2 \times 10^{-8}$ molar. This slight excess of thiocyanate ion is calculated to reduce the silver ion concentration to one fiftieth of its value in the saturated solution. This conclusion is substantiated by electrical measurement of the silver ion concentration. The Volhard titration for silver is based upon the precipitation of silver thiocyanate (see p. 185).

In many problems of this sort there arises a question as to how accurately the calculation need be made. For example, it is desired to calculate what the silver ion concentration would be if solid silver chloride, $S_{AgCl} = 10^{-10}$, were shaken in 100 ml. of 0.0001 M KCl to form a saturated solution. A good approximation may be made by assuming that the chloride ion concentration is unchanged by the slight amount of silver chloride that dissolves. Hence $[Ag^+] = \frac{10^{-10}}{10^{-4}} = 10^{-6}$ molar.[1]

With more complicated substances, the calculations are made with the aid of rather simple algebraic formulae.

Illustration: How much silver and chromate ion will be present in 500 ml. of a saturated solution of silver chromate? ($S_{Ag_2CrO_4} = 2 \times 10^{-12}$). When silver chromate dissolves in pure water, two silver ions enter the solution for each chromate ion. Hence, if the molar concentration of the chromate ion is x, that of the silver ion will be $2x$.

Then

$$[Ag^+]^2\,[CrO_4^{=}] = 2 \times 10^{-12}$$

or

$$(2x)^2x = 2 \times 10^{-12};\ 4x^3 = 2 \times 10^{-12};$$

$x = \frac{10^{-4}}{\sqrt[3]{2}}$, the molar concentration of the chromate ion, and the concentration of the silver ion has twice this value. Hence the concentration of silver in grams per 500 ml. is

$$\frac{1}{2} \times \frac{2 \times 10^{-4}}{\sqrt[3]{2}} \times 107.88 = 0.0086 \text{ g.}$$

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[1] To be strictly accurate, the concentration of chloride ion is increased by an amount x derived from the silver chloride, and at the same time x is the concentration of silver which goes into solution, since silver and chloride ion dissolve in equivalent amounts. Therefore:

$$[Ag^+]\,[Cl^-] = 10^{-10},$$

$$x(10^{-4} + x) = 10^{-10},$$

and the value of $[Ag^+]$ or x, is 0.99×10^{-6} (see Chap. XV). This more precise method of calculation would be an unnecessary refinement here, since only those substances which are extremely insoluble can be used.

Equivalent Weights for Precipitation and Complex-formation Reactions. This subject has already been discussed in Chapter VI, but further elaboration is necessary. The equivalents of substances for precipitation processes are always calculated on the basis of an equivalent of the metallic ion or cation involved in the reaction. The equivalent weight of a metal is the atomic weight divided by the valence.

For univalent metals, Na, K, Ag, etc., eq. wt. = at. wt.; for bivalent metals, Zn, Cd, Hg (ic), Ca, Ba, Sr, etc., eq. wt. $= \frac{\text{at. wt.}}{2}$; and for trivalent metals, Fe, Cr, Al, etc., eq. wt. $= \frac{\text{at. wt.}}{3}$.

For example, silver may be precipitated as silver thiocyanate, silver chloride, etc. The equivalent weights of silver nitrate, amonium thiocyanate, sodium chloride, and potassium chloride, are the respective molecular weights.

In more complicated cases, a similar line of reasoning is followed.

Illustration: Zinc forms the salt, $K_2Zn_3[Fe(CN)_6]_2$, when titrated with potassium ferrocyanide. Three atoms or 6 equivalents of zinc and 2 ferrocyanide radicals are required per molecule of precipitate. To prepare a potassium ferrocyanide solution that is 1 *N* in precipitating power for zinc, $\frac{2K_4Fe(CN)_6}{6}$ or ⅓ of a mole of the ferrocyanide per liter would be needed. This equivalent weight is different from the acidimetric or the oxidation equivalent weight, and would apply only to a particular class of ferrocyanide precipitations.

The equivalents of substances for complex-formation processes are based upon the amount of the metallic ion or cation present in one mole of the complex in much the same manner as precipitation equivalents are based upon the amount of metallic ion or cation in one mole of the precipitate. An important series of complex-formation methods is typified by the reaction which depends upon the addition of standard potassium cyanide solution to a slightly ammoniacal nickel solution:

$$Ni(NH_3)_4Cl_2 + 4KCN \rightleftharpoons K_2Ni(CN)_4 + 4NH_3 + 2KCl.$$

The equivalent of nickel is one-half of its atomic weight. Therefore, a cyanide solution prepared to be 1 *N* in terms of nickel would contain 2 moles of potassium cyanide per liter.

Course of Ion Concentration During a Precipitation or Complex-formation. From the solubility product principle, it is possible to calculate the course of changes in the concentration of the ion that is being precipitated as the precipitation progresses. Take, for example, the values of the chloride ion concentration during the precipitation of 50 ml. of 0.1 *N* sodium chloride with 0.1 *N* silver nitrate. As a fairly close approximation, the chloride ion concentration at points before the end of the reaction may be calculated from the amount of chloride unused, and the total volume. For example, when 45 ml. of silver nitrate has been added, the chloride concentration is: $\frac{5 \times 0.1}{95} = 5.26 \times 10^{-3}$ *N*. At the end-point the chloride concentration is equal to the square root of the solubility product, i.e., $\sqrt{10^{-10}} = 10^{-5}$ *N*. When an excess of silver is present, the chloride ion concentration can be approximated closely by substituting the silver ion concentration, added in excess, in the expression: $[Ag^+][Cl^-] = 10^{-10}$. The values thus found are presented graphically in Fig. 42.

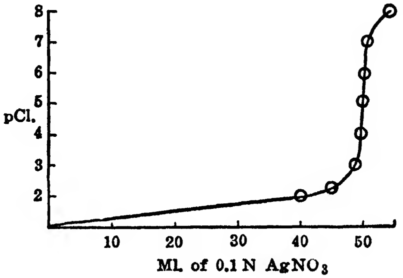

FIG. 42. Graph for the Titration of 50 Ml. of 0.1 *N* NaCl with 0.1 *N* $AgNO_3$. The Effect of Dilution During the Titration Has been Taken into Account. The ordinates are the exponents of the chloride-ion concentration, with negative sign: $Cl^- = 10^{-pCl}$.

The form of graph shown in Fig. 42 may be realized experimentally by electrometric methods. Similar abrupt changes in ion concentration occur at the end-points of complex-formations. The sharpness of the change is greater, the less soluble the precipitate, the more stable the complex, or the more concentrated the two solutions that are brought together.

INDICATORS FOR PRECIPITATIONS OR COMPLEX-FORMATIONS

Many different methods and principles are used in determining end-points in this branch of volumetric analysis.

Formation of a Soluble Compound of Distinctive Color. The formation of such a compound is used to indicate the end-point in the Volhard method for silver. If a considerable amount of ferric nitate (or saturated ferric ammonium alum solution) is added to a solution of silver nitrate, the latter may be titrated with a standard solution of a soluble thiocyanate. After the reaction: $Ag^+ + CNS^- = \downarrow AgCNS$ is complete ($S_{AgCNS} = 1 \times 10^{-12}$), the first drop of thiocyanate in excess reacts with ferric ion, $Fe^{+++} + 6CNS^- \rightleftharpoons Fe(CNS)_6^{\equiv}$, to form complex ferric thiocyanate, and the solution assumes a faint reddish brown coloration.[1]

It is possible to make use of an oxidation-reduction color change if the precipitating reagent is an oxidizing or reducing agent. For example, zinc is precipitated with ferrocyanide containing about 1 per cent of ferricyanide. Ferricyanide oxidizes diphenylamine or diphenylbenzidine to a blue colored compound. As long as zinc ions are present the ferrocyanide ions are practically completely removed from the solution to form the precipitate. The first drop of unused ferrocyanide solution reduces the blue substance to a colorless or faintly greenish one.[2]

Formation of a Second Precipitate of Distinctive Color. The Mohr method for a halide will serve as an illustration of this type of end-point. In the titration of chloride ion with a silver solution an appropriate amount of chromate ion is added to serve as an indicator. The precipitation of silver chloride is essentially complete: $Ag^+ + Cl^- = \downarrow AgCl$, before the precipitation of the silver chromate begins:

$$2Ag^+ + CrO_4^= \rightleftharpoons \downarrow \underset{\text{reddish color}}{Ag_2CrO_4}$$

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[1] Schlesinger and Van Valkenburgh, J. Am. Chem. Soc. **53**, 1212 (1932), have shown that a complex ion $Fe(CNS)_6^{\equiv}$ is probably formed. C. L. French and H. E. Bent ascribe the color to $FeCNS^{++}$ and to $Fe(CNS)_2^+$. (Abstract 23, page P, 10 Cincinnati meeting Am. Chem Soc. 1940.

[2] Method of Cone and Cady, J. Am. Chem. Soc. **49**, 356 (1927).

The theory of the indicator action in this and similar cases is based upon application of the solubility product principle (see Chapter XV, p. 291). The solubility products are $S_{AgCl} = 10^{-10}$, and $S_{Ag_2CrO_4} = 2 \times 10^{-12}$, and the first formation of silver chromate will occur at a point when the silver-ion concentration is in equilibrium with both precipitates:

$$\frac{S_{AgCl}}{[Cl^-]} = [Ag^+] = \sqrt{\frac{S_{Ag_2CrO_4}}{[CrO_4]^=}},$$

and hence:

$$\frac{[Cl^-]}{\sqrt{[CrO_4^=]}} = \frac{10^{-10}}{\sqrt{2 \times 10^{-12}}} = 7 \times 10^{-5}.$$

It is possible to calculate the necessary concentration of chromate ion in order that silver chromate may appear at the theoretical end-point of the reaction where there is a saturated solution of silver chloride. If the concentration of chromate ion were 0.01 *M* at the end-point, then: $[Cl^-] = \sqrt{0.01} \times 7 \times 10^{-5}$ or 0.7×10^{-5} *M*, which is slightly beyond the theoretical end-point (1×10^{-5} *M*). It is apparent that by altering the chromate concentration the precipitate of silver chromate may appear either slightly before or after the theoretical equivalence-point. The total volume of the solution at the end-point will be important; the chromate concentration must be about 0.01 *M* and the solution must be saturated with silver chromate before the reddish coloration can be seen.

Appearance or Disappearance of a Precipitate. The formation or disappearance of a precipitate as an indication of the end-point in complex-formation processes may be illustrated by the following: A trace of silver iodide is added to a nickel solution which is to be titrated with standard potassium cyanide. After the completion of the reaction: $Ni(NH_3)_4Cl_2 + 4KCN \rightleftharpoons K_2Ni(CN)_4 + 4NH_3 + 2KCl$, the turbidity due to silver iodide disappears sharply because the precipitate dissolves to form complex silver cyanide ion:

$$\downarrow AgI + 2KCN \rightleftharpoons KAg(CN)_2 + KI.$$

If mercuric chloride is added to a soluble iodide, a soluble complex salt is first formed: $4KI + HgCl_2 \rightleftharpoons K_2HgI_4 + 2KCl$. The first excess of mercuric ion causes a red turbidity due to a precipitate of mercuric iodide: $HgI_4^{=} + Hg^{++} \rightleftharpoons \downarrow 2HgI_2$. In a reaction of this sort the stability of the complex and the solubility of the precipitate need to be known in order to calculate the sensitiveness of the indication of the end-point. In this case the mercuric iodide appears slightly before the formation of the complex salt is complete, and a correction factor must be worked out for each particular set of conditions.[1]

External Indicators. The presence of the first slight excess of reagent, or the disappearance of the last trace of the ion that is being determined, may often be detected by removing a drop of the clear liquid above the precipitate, and bringing it into contact with a drop of an appropriate reagent, which has been placed in a small depression on a white porcelain plate. This "spot-plate" method has found many applications, as, for example, in the precipitation of zinc with ferrocyanide. The first slight excess of ferrocyanide causes a drop of the solution when brought into contact with a drop of 10 per cent uranyl nitrate solution, to give a brown coloration of uranyl ferrocyanide. In a similar manner the end-point of the precipitation of lead with molybdate ion may be detected by the yellow color which a very dilute molybdate solution gives to a 0.5 per cent tannin solution.

The "spot-plate" technique is not limited to precipitation or complex-formation reactions; it is frequently used in connection with oxidations with bichromate, or other oxidation-reduction reactions (see Chap. XII).

Adsorption Indicators. A new type of indicator for precipitation reactions has been developed by Fajans and his associates in connection with studies on the nature of adsorption.[2] These studies have shown that during a titration, a colloidal precipitate

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[1] A table of corrections for this reaction is given in I. M. Kolthoff's Volumetric Analysis, Vol. II (translated by N. H. Furman), John Wiley & Sons, Inc., New York, p. 269.

[2] K. Fajans and O. Hassel, Z. Elektrochem. **29**, 495 (1923); Fajans and Wolff, Z. anorg. Chem. **137**, 221 (1924); Fajans and v. Beckerath, Z. physik. Chem. **97**, 478 (1921); Fajans and T. Erdey-Gruz, Z. physik. Chem. (A) **158**, 97 (1931). A review has been given by K. Fajans, Newer Methods of Volumetric Chemical Analysis (translated by R. E. Oesper), D. Van Nostrand Co. (1938). Part VII, Adsorption Indicators, pp. 203–250. See also Kolthoff and van Berk, Z. analyt. Chem. **70**, 369 (1927); Kolthoff, *idid.* **71**, 235 (1927); Kolthoff, Lauer, and Sunde, J. Am. Chem. Soc. **51**, 3273 (1929); I. M. Kolthoff's Volumetric Analysis, Vol. I and II (translated by N. H. Furman).

such as a silver halide adsorbs certain types of dyestuff ions more strongly on one side of the equivalence-point than on the other. An appreciable part of the adsorbed dyestuff undergoes a distortion of its electronic system and a sharp change in color results. Dyestuff anions are more strongly adsorbed when an excess of the positive ion of the precipitate is present in the solution than at the equivalence-point or when an excess of the negative ion is present. For example, dyes of the fluorescein series (fluorescein, eosin, erythrosin, etc.) are used in the form of their sodium salts; the anions of these salts are adsorbed more strongly on a silver halide when a slight excess of silver is present in the solution, than in the presence of an excess of halide. Conversely, cations of certain basic dyestuffs, like the rhodamines, for example, are more strongly adsorbed on a colloidal silver halide when a slight excess of the halide ion is present.

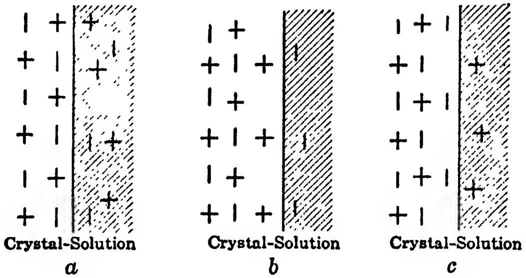

Fig. 43. Surfaces of Neutral, Positive and Negative Colloidal Silver Halide Particles. (Fajans and v. Beckerath, Z. physik. Chem. **97**, 478 (1921).

In Chapter XV, pp. 297-300, the colloidal phenomena that accompany precipitation are mentioned chiefly as tendencies to be counteracted or avoided as far as possible in forming a pure precipitate. The effective action of adsorption indicators depends in some cases upon keeping as much of the precipitate as possible in the colloidal state because this involves a considerable increase in the surface of the precipitate and a greater adsorption of the indicator.

The work of Lottermoser, Fajans and others[1] gives the picture of the colloidal behavior of silver halide in contact with its saturated solution that is represented in Fig. 43, *a*, *b*, *c*, *c*. A neu-

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[1] A. Lottermoser, Journ. prakt. Chem. **72**, 39 (1905); **73**, 376 (1905); J. N. Mukherje, Trans. Far. Soc. **16**, A, 103 (1920).

tral surface is shown in Fig. 43, *a*; a positively charged particle results when an excess of silver nitrate is present, the silver ion being adsorbed as shown in Fig. 43, *b*, the nitrate ion remaining in the layer of the solution near the surface; with excess of potassium halide the surface is negatively charged due to adsorption of halide ions as shown in Fig. 43, *c*; the potassium ions remain in the solution.

These facts are in accord with the rule of Paneth and Fajans, according to which the adsorbability of analogous ions increases in general with decreasing solubility of their compounds with the oppositely charged ion of the precipitate. On the surface of a silver halide the silver and halide ions are much more adsorbed than the potassium or nitrate ions. Of importance in titrations is also the fact that the adsorbability of halide ions on silver halide increases in the order $Cl^- < Br^- < I^-$ and for the anions of fluoresceins in the order:

Least adsorbed ←
Fluorescein, dichlorofluorescein, eosin (tetrabromo), di-iodofluorescein, erythrosin (tetra-iodofluorescein).
→ Most strongly adsorbed.

In this series the given order is that of the decreasing solubility of the corresponding silver salts.

In the titration of a solution of potassium chloride with silver nitrate using fluorescein as indicator, the colloidal particles of silver chloride are at first charged negatively. (Condition shown in Fig. 43, *c*). The indicator remains practically completely in the solution and retains its characteristic greenish yellow fluorescence. After the equivalence-point there is a marked increase in adsorption of the indicator and the dye changes sharply to a pink color which appears to be uniformly distributed through the solution, but is in reality at the surface of the colloidal particles. At this point the condition of the surface of the particles is pictured by Fig. 43, *b*. For the explanation of the action of adsorption indicators three types of mechanism of adsorption were proposed.

Fajans assumed that the ion of the dye is attached to the oppositely charged ions on the surface of the precipitate in a way similar to that shown for the adsorbed ions in Fig. 43 *b* and *c*.

More recent studies by Kolthoff and his associates[1] show that at least in some cases an exchange reaction takes place in connection with the adsorption of the indicator. For example, when bromphenol blue is adsorbed by mercurous chloride, chloride ions are displaced and can be detected in the solution:

$$\underbrace{Hg_2^{++} + Cl_2^{--}}_{\text{surface}} + \underbrace{2\,B.P.B.^-}_{\text{solution}} = \underbrace{Hg_2^{++}(B.P.B.)_2^{--}}_{\text{surface}} + \underbrace{2Cl^-}_{\text{solution}}$$

(where B.P.B.$^-$ represents the anion of the indicator).

Kolthoff assumed that in this exchange the chloride ions of the neutral crystal lattice (Fig. 43, *a*) of the precipitate itself are involved. Vervey[2] makes the chloride ions in the layer of the solution near the surface responsible for the exchange (see Fig. 54, p. 373).

In volumetric analysis the indicator is added in an amount ranging from about 2×10^{-4} to 3×10^{-3} mole per 1 mole of silver halide formed. The color change at the end-point is due to the adsorption of a considerable portion of the indicator; the relative amount varies in different cases. Fajans found that only a part of the adsorbed portion of the indicator underwent a change in color.

Many interesting types of titrations are possible with the aid of adsorption indicators. For example, chloride or bromide ion may be determined in neutral solution with fluorescein as indicator. The results for solutions 0.05 *N* or more dilute, are stated to be more accurate than those by the Mohr titration. Kolthoff, Lauer and Sunde[3] found that dichlorofluorescein may be used as indicator in the titration of slightly acid solutions of chloride with silver ion (*p*H 4.4 or higher). A bromide may be titrated in a solution of *p*H 1 or higher using eosin (tetrabromofluorescein) as indicator. An iodide may be titrated in the presence of a chloride using eosin or dimethyl-di-iodofluorescein as indicator. Rhodamine 6G is an especially good indicator for the titration of silver ion with standard bromide, since the end-point is sharp in the presence of nitric acid up to 0.5 *N* concentration. The

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[1] I. M. Kolthoff, Chem. Rev. **16,** 87 (1935); I. M. Kolthoff and W. D. Larson, J. Am. Chem. Soc. **56,** 1881 (1934); Cf. also I. M. Kolthoff and C. Rosenblum, J. Am. Chem. Soc. **56,** 1264, 1658, 832 (1934).

[2] E. J. W. Vervey, Kolloid Z. **72,** 187 (1935).

[3] Kolthoff, Lauer and Sunde, J. Am. Chem. Soc. **51,** 3273 (1929).

sum of iodide and chloride can be determined very satisfactorily with tartrazine[1] as indicator.

The effect of foreign salts depends partly on their coagulating action on the colloidal precipitate, decreasing its surface and hence the amount of adsorption of the indicator. This effect increases with the magnitude of the charge on the foreign ions and is therefore most noticeable with multi-valent ions. Of importance may also be the displacement of the indicator ion by the foreign ions present. The disturbing action of hydrogen ions in some cases is due not only to the factors mentioned for the salts but also to the formation with the anion of the indicator of an undissociated acid which interferes with the adsorption of the anion of the indicator.

These disturbing effects of foreign ions are of less importance in the case of phenosafranine as indicator[2] the action of which shows, according to Fajans and Weir,[3] a different mechanism than those of other adsorption indicators. Phenosafranine being a basic dyestuff is adsorbed on silver chloride or silver bromide more intensely in the presence of an excess of halide ion than when an excess of silver ion is present. But this difference is not very pronounced for a small excess of those ions and not essential for the color change at the equivalence-point. If an excess of halide is present phenosafranine is adsorbed on the coagulated precipitate with nearly the same reddish color that it shows in the solution. When, in the course of titration, a small excess of $AgNO_3$ is reached, the color of the adsorbed (not of the dissolved) dyestuff changes very sharply to blue in the case of silver bromide or to lilac on silver chloride. For this color change the presence not only of silver ions but also of nitrate ions is essential,[4] the blue color being due to a complex of phenosafranine and silver nitrate, adsorbed on the silver halide. Since the color change is observed on the coagulated precipitate itself, the co-

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[1] First used for titrations of silver with bromide or chloride by A. J. Berry and P. J. Durrant. The Analyst **55**, 613 (1930). See also the review of Fajans cited on p. 169.

[2] Found suitable as adsorption indicator independently by Fajans and Weir, (Diss. Munich 1926) and Berry and Durant, The Analyst **55**, 613 (1930); Berry, *ibid.* **57**, 511 (1932); **61**, 315 (1936).

[3] See the review of Fajans.

[4] Silver perchlorate or silver fluoride cannot be used for titration.

agulating action of foreign cations, including heavy metals, does not interfere. The color change is easily reversible. It is possible to perform the titration in the presence of large amounts of cadmium, lead, zinc, and also some colored ions like iron, chromium, etc. Hydrogen ions below the concentration of about 0.2 *N* do not change the position of the color change and make it only a little less distinct.

Adsorption indicators have been proposed not only for titration of silver, halides, CN^-, CNS^-, but also for a number of other cases like Pb^{++}, $Hg_2{}^{++}$, Ba^{++}, $CrO_4^=$, $C_2O_4^=$.

Equal Turbidity Method. At the end-point of a precipitation there should be a saturated solution of the precipitate in contact with the solution of the other substances that are formed. If potassium chloride and silver nitrate have been brought together, there results at the equivalence-point, provided equilibrium has been reached, a solution of potassium nitrate which is saturated with silver chloride. If equivalent volumes of silver nitrate and potassium chloride solutions, respectively, are added to separate measured volumes of the clear supernatant solution, equal turbidities of silver chloride should be produced. If equal turbidities are not found, the titration is continued with potassium chloride or silver salt solution to the point of equal turbidities. This is the classical Gay-Lussac method for silver, which has remained one of the most exact volumetric methods for over a century. A refined modification of this procedure is still used for determining silver in the mints of certain governments.

Neutralization Indicators in Hydrolytic Precipitation Reactions. If the salt of a weak base and strong acid, or the salt of a weak acid and strong base, can be used to precipitate an ion, then there is a possibility that there will be a sharp change in hydrogen ion concentration at the end-point, and hence, that a neutralization indicator may be used. For example, sodium palmitate (soap) solution is alkaline to phenolphthalein. If a neutral calcium solution is titrated with this reagent, the solution does not become alkaline to phenolphthalein indicator until the precipitation of the calcium as the palmitate is complete and a slight excess of the reagent has been added. This method is of importance in determining calcium and magnesium ("hardness" of water).

The reagents, sodium carbonate, potassium cyanide, and potassium chromate are frequently employed in hydrolytic precipitation or in complex-formation reactions.

It might be anticipated that the completion of the formation of an insoluble hydroxide like ferric or magnesium hydroxide, with sodium hydroxide as reagent, could be detected with a neutralization indicator. This type of titration process is not, however, of general utility because basic salts of indefinite composition are almost invariably formed. Pure solutions of cupric, nickel, or cobalt salts can be analyzed fairly accurately by adding a measured excess of standard alkali solution, heating, cooling, filtering, and titrating the excess of alkali in the filtrate with a standard acid.

Evaluation of Analyses. The general formulations which have been given in Chapter VIII apply to precipitation analyses.

Illustration: The silver in the solution of an alloy was determined by precipitation with standard ammonium thiocyanate solution (Volhard's method). A 0.4060 g. sample of the alloy required 22.30 ml. of 0.1016 N ammonium thiocyanate solution. The percentage of silver is found as follows:

$$\text{Weight of silver} = \overset{\text{ml. of } N \text{ soln.}}{22.30 \times 0.1016} \times \overset{\text{m.e.}}{\frac{107.88}{1000}}.$$

Weight of sample: weight of silver = 100 : per cent silver.

$$\text{Per cent silver} = \frac{22.30 \times 0.1016 \times 0.10788}{0.4060} \times 100 = 60.20.$$

Review Questions and Problems

1. Check the calculation of the following points of Fig. 42, p. 166: the chloride-ion concentration after adding 40.49, 49.90 and 49.95 ml. respectively of 0.1000 N silver nitrate.

2. How much crystallized potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3H_2O$) is needed for 2.000 liters of a solution that is to be 0.2000 N as a precipitating agent for zinc? How much potassium cyanide is needed for 5.000 liters of a solution that is 0.05000 N for the complex-titration reaction for nickel?

3. Taking the solubility product of silver chloride to be $S_{AgCl} = 10^{-10}$ and $S_{Ag_2CrO_4} = 2 \times 10^{-12}$, at what chloride-ion concentration would the precipitation of silver chromate begin in each of the following cases: (a) $[CrO_4^{=}] = 10^{-4}\ M$; (b) $[CrO_4^{=}] = 10^{-2}\ M$; and (c) $[CrO_4^{=}] = 10^{-1}\ M$? Ans. (a) $7 \times 10^{-7}\ M$; (b) $7 \times 10^{-6}\ M$; (c) $2 \times 10^{-5}\ M$.

Which of these concentrations of chromate is most suitable for the indicator in the Mohr titration?

4. List the methods of finding the end-point of the titration of chloride with silver in the order of decreasing convenience. Which of the methods are interfered with (a) By foreign colored matter, e.g., chromic ions, dyestuffs, etc? (b) By high concentrations of calcium, aluminum or other multivalent ions? (c) By the presence of acids, e.g., nitric, perchloric or sulfuric?

5. With solid silver chloride and thiocyanate in contact with a solution, calculate the concentration of chloride ion at the point where that of the thiocyanate ion is 10^{-5} *M*.[1] Use $S_{AgCl} = 10^{-10}$; $S_{AgCNS} = 10^{-12}$.

6. If the silver chloride were not filtered off in a Volhard titration for chloride, before titrating the excess of silver ion with thiocyanate solution, calculate the error in ml. of 0.1 *N* solution per 200 ml. of solution, due to the solubility of silver chloride in a thiocyanate solution as calculated in problem 5. Ans. 2.0 ml. (The actual error found by experiment is somewhat greater than 2 ml.).

7. How may the Mohr method be applied to the determination of the chloride in a solution of hydrochloric acid?

8. Given: $H^+ + CrO_4^{=} \rightleftharpoons HCrO_4^-$; $K = \frac{[H^+][CrO_4^{=}]}{[HCrO_4^-]} = 10^{-7}$, calculate the ratio of $[HCrO_4^-]:[CrO_4^{=}]$ at *p*H 5, 6 and 7 respectively. Ans. 100; 10; 1.

9. If enough potassium chromate is added to a solution to make its gross concentration 0.02 molar, what will be the effective concentrations of the chromate ion ($CrO_4^{=}$) at *p*H 5, 6, 7 and 8 respectively?

10. Given $S_{AgOH} = 2 \times 10^{-8}$, at what *p*H will silver hydroxide be precipitated when $[Ag^+]$ is 10^{-5} *M*? Why is a *p*H of 10 considered as the upper limit for the Mohr titration rather than the *p*H here calculated?

PROCEDURES

Among precipitation reactions most commonly used in analytical work may be mentioned the following:

$$(1)\quad NaCl + AgNO_3 = \downarrow AgCl + NaNO_3.$$

This will be discussed in detail later.

$$(2)\quad 3ZnCl_2 + 2K_4Fe(CN)_6 = \downarrow K_2Zn_3(Fe(CN)_6)_2 + 6KCl.$$

In this reaction, the end-point is easily determined by using a uranyl salt as external indicator, which, with an excess of ferrocyanide, gives the solution a chocolate color by forming insoluble

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[1] This is roughly the concentration of thiocyanate ion that is just sufficient to give a visual indication with the usual amount of ferric indicator present (Volhard titration).

uranyl ferrocyanide, $(UO_2)_2Fe(CN)_6$; or, less satisfactorily, by using as internal indicator a ferric salt, which gives a blue color of ferric ferrocyanide. Diphenylbenzidine and diphenylamine may be used as oxidation-reduction indicators (p. 199).

$$(3)\ Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 = \downarrow PbMoO_4 + 2NH_4C_2H_3O_2.$$

A solution of tannin in water or of pyrogallol in chloroform used as external indicator gives a yellow or brown color with an excess of molybdate.

$$(4)\ AgNO_3 + KCNS = \downarrow AgCNS + KNO_3.$$

Ferric sulfate or ferric nitrate added to the solution gives the red color of complex ferric thiocyanate, $Fe[Fe(CNS)_6]$, with excess of thiocyanate. This method is capable of very wide application, for it may be used indirectly to determine those substances that form insoluble silver salts, either by dissolving the precipitated salt in nitric acid and titrating the silver ion in the solution, or by adding an excess of standard silver nitrate and titrating back with thiocyanate.

$$(5)\ 2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3.$$

This reaction will be discussed in detail later.

$$(6)\ (NH_3)_4NiCl_2 + 4NaCN = Na_2Ni(CN)_4 + 2NaCl + 4NH_3.$$

The end-point is the disappearance of a slight opalescence of silver iodide, which is insoluble in ammonia but soluble in an excess of the cyanide, thus:

$$(6a)\ \downarrow AgI + 2NaCN = NaAg(CN)_2 + NaI.$$

Since iron does not interfere, and is kept in solution by causing it to react with a citrate, this method is widely used for the determination of nickel in steel.

$$(7)\ 2Cu(NH_3)_4(NO_3)_2 + 7NaCN + H_2O = Na_4Cu_2(CN)_6 + NH_4CNO + 6NH_3 + 3NaNO_3 + NH_4NO_3.$$

In an ammoniacal copper solution, the disappearance of the blue color marks the end-point but the composition of the complex cyanide varies somewhat according to conditions. In this reaction, one molecule of the cyanide acts as a reducing agent and is oxidized to a cyanate, a complex cuprous cyanide being formed. One NaCN reduces $2Cu^{++}$. This method is very empirical. In practice, the iodide and thiocyanate methods are more satisfactory for copper.

Preparation of 0.1 *N* Silver Nitrate Solution. Since silver has a valence of one, its equivalent and that of silver nitrate are the atomic and molecular weights, respectively, and one liter of 0.1 *N* solution will contain 10.788 g. of silver or 16.989 g. of the nitrate; 500 ml., the amount made up, will contain 8.4945 g. of silver nitrate. The solution may be prepared by weighing the proper amount of metal and dissolving it in nitric acid, or where the presence of acid is undesirable, as in this case, by weighing out the requisite amount of silver nitrate, which can be obtained very pure, and which can even be fused without decomposition if care is taken to exclude all organic matter, dust, and other reducing substances. The former method is more exact.

Procedure. Dry a clean, stoppered weighing bottle in the oven at 100-110° C. for an hour or longer. Cool and weigh it. Add 8.50 g. of silver nitrate, dry the bottle and its contents in the oven for at least two hours, and then cool and weigh again. In this way the weight of the dry silver nitrate is obtained. Handle the bottle with a cloth or chamois skin. The salt will lose a few milligrams on drying and its color may darken somewhat. Transfer the silver nitrate to a small beaker and rinse the bottle thoroughly with distilled water. Transfer the clear solution to a 500 ml. volumetric flask and dilute to the mark at room temperature. If the weight of silver nitrate is not exactly the theoretical, calculate the normality. Any opalescence in the solution is due to traces of a chloride in the distilled water or to unclean vessels.

DETERMINATION OF CHLORIDE IN A SOLUBLE CHLORIDE

Mohr's Method. *Principle.* The precipitation of chloride, bromide, cyanide, thiocyanate, and other ions in the form of insoluble silver salts can be made the basis of a very accurate method of analysis if a suitable means can be found to determine when precipitation is complete. This can be done by allowing the precipitate to settle and testing the clear solution by the addition of more silver nitrate. Such a procedure, although it gives excellent results, is extremely tedious and requires hours for its completion. If it were possible to find a dark colored insoluble silver salt *more soluble than the one formed by precipitation*, the former would not precipitate until practically all of the less soluble compound was precipitated.[1] Such salts are the dark red silver chromate, Ag_2CrO_4, and the chocolate colored silver arsenate, Ag_3AsO_4, both of which are much more soluble than silver chloride. Of these two, the chromate gives a better end-point and is generally used. In 100 ml. of water at room temperature about 4.2 mg. of silver chromate will dissolve as compared with 0.16 mg. of silver chloride. In the presence of an excess of chromate ion this value is considerably reduced. On account of this solubility, an appreciable excess of silver nitrate is required to give a concentration of silver ion just sufficient to precipitate silver chromate, and still more silver nitrate is required to precipitate enough silver chromate so that its color will be visible. This excess will be smaller as the concentration of chromate increases, but with an increase of the latter, the yellow color of the solution soon becomes deep enough to mask somewhat the red color. It is necessary, therefore, to adopt a moderate concentration—about 0.05 g. of potassium chromate per 100 ml. of solution. The excess of 0.1 N silver nitrate required to give an end-point under these conditions is from 0.05 to 0.1 ml. It is advisable to determine this quantity definitely by running a "blank"—the solution containing no chloride, but only the chromate and some inert white precipitate in suspension, such as calcium carbonate. Enough silver nitrate is added to match the color obtained in the titration. The amount of this blank is then subtracted from the amount used in the titration. The volumes of the two solutions at the end of the titration should be approximately the same. The change in color is more distinct in yellow light. It is very important that the calcium carbonate be free from chloride, for otherwise the blank will be too high. If there is any doubt of its purity, some of it should be dissolved in nitric acid and tested.

The titration consists in adding silver nitrate with constant

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[1] This statement applies to reactions in which co-precipitation does not occur.

stirring until all the chloride ion is precipitated (Equation (1)) and silver chromate just begins to form:

(8) $K_2CrO_4 + 2AgNO_3 = \downarrow Ag_2CrO_4 + 2KNO_3$

as shown by a reddish or brownish tinge in the solution.

Anything that increases the solubility of silver chromate decreases the delicacy of the end-point. Since even a very slightly acid solution has this effect, it is evident that the solution should be neutral (pH between 6.3 and 10). If only very slightly alkaline, no error is introduced; if more alkaline, silver oxide or carbonate will precipitate instead of silver chromate. A simple method of making the solution neutral is to add an excess of calcium carbonate, which dissolves as long as acid is present, but the excess of which does not make the solution alkaline. Chlorides of many elements, such as aluminum, form precipitates when the solution is neutralized; others are colored; other elements form insoluble chromates such as barium chromate as soon as the indicator is added. It is evident, therefore, that this method is of very limited applicability, and is suitable only for such chlorides as those of magnesium, calcium, potassium, sodium and ammonium. Obviously nothing else which is precipitated by silver can be present.

The samples given out are neutral chlorides and need not be tested for neutrality.

Errors. The principal error, that involved in the end-point, has already been discussed. The greater the volume of the solution, the more silver nitrate is required to give the end-point. The error due to acidity and alkalinity has also been mentioned.

Another source of error lies in the fact that the precipitate of silver chromate, formed where the drop of silver nitrate strikes the solution, reacts more slowly with the chlorides than a solution would:

(9) $\downarrow Ag_2CrO_4 + 2NaCl = \downarrow 2AgCl + Na_2CrO_4.$

The solution should therefore be agitated for a minute or two to make sure that the color is permanent. The method gives still better results if, when a faint end-point appears, the solution is boiled for five minutes, cooled to 20° C. or lower, and the titration completed.[1]

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[1] Meldrum and Forbes, J. Chem. Ed. 5, 205 (1928).

Other Applications. Bromide but not iodide ions in soluble neutral salts are titrated in the same way; some other ions might be. Silver is never determined by this process, since it would be necessary to add the unknown solution from a buret, and since a more efficient reaction is available (Equation (4)).

Procedure. Weigh out accurately into 250 ml. conical flasks samples of 0.35-0.45 g. and dissolve each in 50 ml. of water. Add 1 ml. of 5 per cent potassium chromate, K_2CrO_4, solution (Why could not the bichromate be used?) and titrate as described in the next paragraph. Or, weigh out two samples of 2 to 2.5 g. each; dissolve and dilute to 250 ml. in volumetric flasks. To each of two 250 ml, conical flasks add 1 ml. of a 5 per cent solution of potassium chromate. Draw off into these flasks approximately 45 ml. portions of the first sample and titrate as follows.

Add 0.1 *N* silver nitrate solution until the red color formed by the addition of each drop begins to disappear more slowly—an indication that most of the chloride has been precipitated (Equation (1)). Add to another flask containing the chromate indicator the same volume of water as present in the first one, then enough calcium carbonate free from chloride (side-table) so that the turbidity in each liquid seems to be the same when they are rotated. About half the amount of calcium carbonate that can be heaped upon a dime will usually be required. This liquid is the "blank." Continue the titration of the unknown sample until a faint but distinct change in color occurs, resulting from the presence of a trace of silver chromate (Equation (8)). When aliquot parts are used and the end-point is overstepped, more of the chloride solution may be added and the titration continued. Be sure that the end-point is permanent; the color should not be dark—just noticeably different from that of the blank containing no silver chromate. Add to the blank enough silver nitrate so that the colors of the two liquids exactly match. From 0.05 to 0.1 ml. will be required, depending upon how dark an end-point was used; the colors can be matched very closely—within 0.02 ml. This volume is the "blank" for the end-point, and is to be deducted from the volume of silver nitrate used in the titration. The calcium carbonate is added merely to aid in matching color tints, since both vessels then contain a white precipitate. If the blank is too high it may be due to the presence of a chloride in the carbonate. (Test it.)

Now titrate the solution in the second conical flask. Prepare another blank, adding approximately that volume of water which will be present at the end of the titration. When the titration is finished, compare the colors of the unknown liquid and of the blank and find the amount of the blank as before. If the two titrations do not agree within 0.1 or 0.15 ml. after reduction to volumes required for the same size of sample, another titration should be made. When a titration is finished, pour the silver chloride precipitate into the large bottle provided for that purpose on the side-table. By matching colors as directed above, the results should check very closely. Otherwise they may vary considerably.

Calculation of Results. Since one atom of chlorine unites with one of silver, the equivalent of the former is its atomic weight, and 1 ml. of N silver nitrate corresponds to 0.03546 g. of chlorine. Convert the volume of silver nitrate used into its equivalent of normal solution and calculate the percentage of chlorine in the usual way, after finding the weight of sample titrated as previously directed.

Fajans' Method. 1. *Phenosafranine as adsorption indicator.* According to the explanation given on p. 173 the very sharp and easily reversible color change of phenosafranine is to be observed on the coagulated precipitate of the silver halide itself. The change is due to the addition of very small amounts of silver nitrate to that portion of the basic dyestuff which is adsorbed on the precipitate in the presence of excess of halide and not displaced by an excess of silver. For the determination of a chloride the procedure in preparation of the standard solution and in the determination itself differs from that described under 2 in the following respect: Do not add dextrin. Use for the 45 ml. of the 0.1 N sodium chloride solution 6 or 7 drops of 0.2 per cent phenosafranine solution (1 or 2 drops per millimole of silver halide). While adding the silver nitrate solution, shake the flask *vigorously,* especially near the equivalence-point, in order to make the coagulation of the precipitate as complete as possible and to make the comparison of the color of the precipitate and that of the solution easier. In the presence of an excess of chloride the adsorbed and the dissolved dyestuff are pink; an excess of silver changes the color of the precipitate to lilac. Observe the precipitate on the bottom of the flask from below. For this purpose a small mirror is convenient. In standardizing the solution note the appearance of the end-point by reversing the color change several times by addition of the sodium chloride or the silver nitrate solution. One drop of the 0.1 N solutions gives a very distinct color change.

2. *Fluorescein or dichlorofluorescein as adsorption indicator. Principle.* This was discussed in detail on p. 169 ff. The amount of the anions of these dyestuffs adsorbed on colloidal or precipitated silver chloride varies greatly during the titration as the composition of the solution changes from an excess of halide to excess of silver. The adsorption is connected with a sharp change of color. Fluorescein is a very weak acid, dichlorofluorescein is a little stronger; since the anions must be adsorbed the solution should be neutral with the first indicator; with the second the pH should be not less than 4. The adsorption is increased by a large surface of the silver chloride, therefore conditions which favor coagulation, such as higher temperature or multivalent ions, make the color change less distinct. Dextrin, acting as a protective colloid, has the opposite effect by keeping the precipitate in the sol form; it is also easier to observe the color change in the whole apparently homogeneous colloidal system than when the dyestuff is transferred from the solution to the coagulated precipitate. Silver chloride containing adsorbed dye is sensitized to light, therefore titration in bright light gives no satisfactory color change. Samples for comparison of the color change in different titrations should be kept only for a short time and in the dark. Calcium carbonate may be used to neutralize moderate amounts of free acid, followed by the addition of a little dextrin to offset the coagulating effect of the calcium ion. Neutralization by means of chloride-free sodium hydroxide, or nitric acid as required, using phenolphthalein as indicator, is also recommended. Vigorous swirling of the liquid during the titration is advantageous. The first permanent change from yellowish white to a salmon pink tinge in the suspension and in the settled precipitate is taken as the end-point. The phenomena are reversed on the addition of a chloride. Accurate results are readily obtainable. Dichlorofluorescein gives a sharper color change than fluorescein.

Preparation of Standard Solutions. Dry six grams of sodium chloride (analytical reagent grade) in the electric oven at 100-

110° C. for two hours. After cooling in the desiccator for an hour, weigh out 5.846 g., and dissolve in water. Transfer the solution to a calibrated liter flask, dilute to the mark, mix thoroughly, and pour the solution into a dry bottle provided with a tightly fitting rubber stopper. The amount of sodium chloride mentioned is that required for 1000 ml. of exactly 0.1 *N* solution, but the actual normality may vary somewhat. Half a liter, or, if necessary, one liter of 0.1 *N* silver nitrate should be prepared as previously described and should be standardized against the sodium chloride solution as follows: By means of a buret, measure into 250 ml. conical flasks approximately 45 ml. portions of the 0.1 *N* sodium chloride solution. Add to each of these samples 5 ml. of 2 per cent dextrin solution, 10 drops of 0.1 per cent dichlorofluorescein in 70 per cent alcohol, and titrate with the silver nitrate solution in a diffuse light, while rotating the flask rapidly to stir the contents thoroughly. If preferred, 1 ml. of a 0.2 per cent alcoholic solution of fluorescein or an aqueous solution of its sodium salt may be substituted for the dichlorofluorescein. Near the equivalence point, the local development of a pink color on the addition of a drop of silver nitrate solution becomes more and more pronounced. Also, the silver chloride is likely to coagulate noticeably. Finally, at the end-point, the entire solution or suspension changes sharply in color to a distinct salmon tint, and the precipitate which settles has a pink or heliotrope shade. Results agreeing within 2 parts per 1000 should be obtained for the normality of the silver nitrate, which is calculated as directed in Chapter VIII, p. 140.

To become familiar with the appearance of the end-point a preliminary experiment may be performed. Just before reaching the equivalence-point pour approximately half the solution into a second flask. Add one drop of silver nitrate to one of the flasks and compare them. If the two flasks show no definite difference in color, mix the two parts together and repeat the division and mixing after the addition of each drop, until one drop causes a distinct change from a pale pinkish yellow to pinkish. When this point is reached and the two parts are combined, one drop of the 0.1 *N* sodium chloride solution should give a detectable change to a paler color and then one drop of the silver nitrate again a change to a pinker color. This is then the right change to be observed in normal titrations without dividing the solution.

Volhard Method for Silver Applied to the Halogens, etc. It has been shown that the methods just described are of limited applicability. Another not open to these objections is more frequently used. This method is indirect because it is really a method for silver, based upon the fact that any method of titrating silver can be utilized for determining the halides, etc., by adding an excess of standard silver solution to precipitate the salt, and then titrating this excess. The best reaction is that occurring between silver ion and a thiocyanate (Equation (4)), the end-point of which is very sharp. In the case of a chloride, the method is as follows:

Procedure. Add to the solution of the chloride, which may be either an acid or a neutral solution, an excess of standard silver nitrate. Shake to coagulate the precipitate, filter and wash (Equation (1)). Acidify the filtrate with nitric acid, add, for each 100 ml. of solution, 2 ml. of a saturated solution of ferric alum containing a little nitric acid and free from chloride ion. Run in potassium thiocyanate which has been standardized against silver nitrate (Equation (4)) until a faint brownish red tinge of $Fe(CNS)_6^{\equiv}$ appears. Equation for end-point:

$$(10)\quad 2Fe(NO_3)_3 + 6KCNS = Fe[Fe(CNS)_6] + 6KNO_3.$$

By subtracting the volume of the thiocyanate from that of the silver nitrate, after each volume has been multiplied by the appropriate normality, the volume of silver nitrate required for determining the chloride is obtained. This method is applicable to any chloride, bromide, iodide, etc., the color of which is not deep enough to obscure the end-point.

It is necessary to filter off the silver chloride, since it is more soluble than silver thiocyanate and therefore would react thus:

$$(11)\quad \downarrow AgCl + KCNS = \downarrow AgCNS + KCl,$$

giving low results. Since silver bromide and iodide are less soluble than silver thiocyanate, they cannot react with potassium thiocyanate, and therefore do not need to be filtered off.

The necessity for filtering off the silver chloride may be eliminated by surrounding it with a film of nitrobenzene.[1] One ml. of the latter is added for each 0.05 g. of chloride. After add-

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[1] Caldwell and Moyer, Ind. Eng. Chem., Anal. Ed., 7, 38 (1935).

ing excess of silver nitrate the solution is shaken vigorously until the silver chloride settles out in large flakes, but a perfectly clear supernatant liquid is not necessary. The excess of silver is then titrated as usual.

Other Applications. This process can be applied to any one of the many ions forming insoluble silver salts. Silver nitrate is therefore one of the most valuable standard solutions for precipitation reactions. The only disadvantage of this method is that it requires two standard solutions; both, however, are perfectly stable. Among the acids which form insoluble silver salts are: HCl, HBr, HI, HIO_3, HCN, $HCNS$, H_2CrO_4, H_3PO_4, H_3AsO_4, H_2S, $H_2C_2O_4$, H_2CO_3, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$. Any of these salts, if soluble in nitric acid, as, for example, Ag_3AsO_4, Ag_3PO_4, Ag_2S, $Ag_2C_2O_4$, Ag_2CO_3, may be dissolved in it and the silver ion titrated directly with standard thiocyanate. In this case only one standard solution, potassium thiocyanate, is required.

Procedure for Determination of Silver in Alloys. Weigh out a 0.5 g. sample of the silver alloy, dissolve it in 15 ml. of a mixture of equal parts of water and concentrated nitric acid. Boil the solution until all nitrous fumes are expelled, cool it and dilute to 50 ml. Add 2 ml. of a saturated solution of ferric alum, free from chloride, and titrate with standard thiocyanate, until a faint brownish red tinge of the ferric complex appears. From the volume of solution used calculate the percentage of silver in the alloy.

DETERMINATION OF CYANIDE BY TITRATION WITH SILVER NITRATE

Principle. When a solution of silver nitrate is added to that of a cyanide, no precipitate is formed, the silver cyanide dissolving in an excess of the cyanide to form the complex ion

$$Ag(CN)_2^- : \quad 2NaCN + AgNO_3 = NaAg(CN)_2 + NaNO_3.$$

(Equation already given on page 177). When enough silver has been added to unite with all of the cyanide in this way, any more will react with this complex salt, precipitating silver cyanide:

$$(12)\quad NaAg(CN)_2 + AgNO_3 = \downarrow Ag(Ag(CN)_2) + NaNO_3.$$

The formation of this precipitate indicates that the end-point has been reached. Not only silver cyanide but all other silver salts except the sulfide are readily soluble in an excess of a solution of an alkali cyanide; therefore chloride, bromide, iodide ions, etc., do not interfere. The only difficulty in obtaining a sharp end-point lies in the fact that the silver cyanide is often precipitated in a curdy form which does not readily redissolve. The precipitation of silver cyanide at the end-point can be avoided by the addition of ammonia, in which it is readily soluble:

(13) $\downarrow 2AgCN + 4NH_4OH = 2Ag(NH_3)_2CN + 4H_2O.$

Then a little potassium iodide, if added to the solution before the titration with silver nitrate is commenced, will serve to indicate the end-point, thus:

(14) $Ag(NH_3)_2CN + KI = \downarrow AgI + KCN + 2NH_3.$

During the titration any silver iodide which would have a tendency to form will be kept in solution by the excess of cyanide always present until the end-point is reached:

(15) $AgI + 2NaCN = NaAg(CN)_2 + NaI.$

When the last of the cyanide has been removed from the solution at the end-point, an opalescence caused by silver iodide will appear. This is due to the fact that the first drop in excess of the silver nitrate solution will react with the potassium iodide present to form silver iodide:

(16) $AgNO_3 + KI = AgI \downarrow + KNO_3.$

The cyanide in which this precipitate was soluble throughout the titration is no longer present to keep it in solution, and it does not dissolve in the ammonium hydroxide as does silver cyanide. When viewed against a black background this end-point is easy to see and the method gives excellent results.

Since the cyanides of sodium and of potassium are both somewhat deliquescent and cannot be properly put up in dry form for analysis, the cyanide sample will be given out in the form of a solution. This slowly decomposes on standing, giving ammonia, formic acid and other products, and must therefore be titrated within a day or two of the time it is prepared.

Other Reactions Using Cyanide. The reaction described above can be reversed and used to determine silver, particularly in silver halides, by adding excess of standard cyanide and titrating back with standard silver nitrate.[1] The thiocyanate method is more convenient in most other cases, and is more commonly used.

The formation of complex cyanides makes possible the volumetric determination of several other metals, especially nickel and copper (Equations (6) and (7)).

Procedure. Clean and dry a 125 ml. conical flask provided with a cork. Mark the flask with your name and desk number and leave it with the assistant to be filled with the cyanide solution. All these solutions, because of their instability, will be given out at the same time and must be analyzed and the results reported within a few days, regardless of what other work may be in progress. Stop work on other determinations until this determination is completed. Weigh two clean, dry conical flasks with stoppers. Pour into each about 8 or 9 ml. of the cyanide solution, stopper and weigh again. Add to each sample 10 ml. of a solution of potassium iodide and ammonia, which contains 10 g. of potassium iodide and 300 ml. of concentrated ammonia (density 0.90) per liter, so that 3 ml. of ammonia and 0.1 g. of potassium iodide are present during each titration. The solution must be perfectly clear before titration.

Run in 0.1 *N* silver nitrate with constant swirling until a barely visible opalescence is observed when the liquid is viewed against a black background (Equations (5) and (13)). If the end-point is overstepped, repeat the titration on another sample; the results should check within 0.02 or 0.03 per cent, since the solutions are rather dilute. The results are graded ten times as closely as the chloride analyses.

When the titration is finished, empty the contents of the flask into the bottle provided for silver residues. All waste silver solutions are to be poured into this bottle and not to be thrown away.

Calculation of Results. From equation (5) it is seen that 2KCN react with 1 Ag, from which it follows that the equivalent

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[1] See also J. S. Pierce and J. L. Coursey, Ind. Eng. Chem., Anal. Ed. **4**, 64 (1932).

of CN is twice its molecular weight or 52.03. One ml. of normal silver nitrate is therefore equivalent to 0.05203 g. of CN. Calculate the percentage of CN in the solution in the usual way using the normality of silver nitrate calculated from its weight.

Review Questions and Problems

1. Write equations for the separation and volumetric determination of zinc and silver in an alloy of the two metals. Suggestion: first separate silver as sulfide.

2. Write equations for the separation and volumetric determination of copper and lead in an alloy of the two metals. Suggestion: lead sulfate is soluble in ammonium acetate.

3. Suggest a volumetric method for the determination of silver in silver bromide.

4. In a sample weighing 1.0000 g. the arsenic is oxidized to arsenate and precipitated as silver arsenate, Ag_3AsO_4. This, when dissolved in nitric acid, required 50.00 ml. of 0.1100 *N* thiocyanate solution. What percentage of arsenic in the sample? (Do not use the atomic weight of silver.)

Ans. 13.73 per cent.

5. One gram of pure KIO_x after reduction to iodide required 46.72 ml. of 0.1000 *N* silver nitrate for precipitation. Calculate the value of x.

6. What is the residual concentration of silver ion in the precipitation of silver chromate with potassium chromate when barium chromate begins to form if the concentration of barium ion at this point is 0.040?

Ans. 0.020 *M*.

7. In the precipitation of calcium fluoride with calcium ion what is the residual concentration of fluoride ion when calcium carbonate begins to precipitate if the concentration of carbonate ion at this point is 0.1000 *M* and hydrolysis effects are disregarded?

8. Calculate the mg. of bromide ion per liter remaining unprecipitated at the end-point in the titration of bromide with 0.100 *N* silver nitrate by Mohr's method if the solution is 0.020 *M* with respect to potassium chromate.

Ans. 0.0032.

9. If 50.00 ml. of 0.1000 *N* silver nitrate is used in titrating 35 ml. of cyanide solution, and 10.00 ml. of the latter is used in titrating the nickel in a 1.000 g. sample of steel, what is the percentage of nickel in the steel?

10. One gram of a mixture containing only sodium bromide and sodium iodide requires 88.03 ml. of 0.1000 *N* silver nitrate for complete precipitation of both halogens. What percentage of each salt is present? Suggestion: if $x =$ grams of NaI and $1 - x =$ grams of NaBr, then x grams of NaI require how many ml. of $AgNO_3$, etc.?

11. Write equations showing how to determine cyanide and thiocyanate in a mixture containing also inert salts.

CHAPTER X

OXIDATION-REDUCTION REACTIONS

INTRODUCTION AND THEORETICAL CONSIDERATIONS

Standard solutions of either oxidizing or reducing agents are used in this field of volumetric analysis. Numerous oxidizing and reducing agents of varying intensity of action are available and much information has been accumulated regarding the proper fields of their application. Potassium permanganate, for example, is one of the most powerful of the oxidizing agents, while iodine is one of the weakest ones. The oxidizing agents that are very frequently used in standard solutions are potassium permanganate, $KMnO_4$, potassium bichromate, $K_2Cr_2O_7$, ceric sulfate, $Ce(SO_4)_2$, potassium iodate, KIO_3, potassium bromate, $KBrO_3$, and iodine.[1] The reducing agents that are frequently used in a similar manner are ferrous sulfate, $FeSO_4$, sodium thiosulfate, $Na_2S_2O_3$, sodium arsenite, $NaAsO_2$ (or Na_3AsO_3), and oxalic acid. The still more powerful reducing agents, titanous salts, $TiCl_3$ or $Ti_2(SO_4)_3$, and chromous salts, $CrCl_2$ or $CrSO_4$, are so easily oxidized that air must be excluded from the solution that is titrated as well as from the reagent.

Few of the reagents that have been mentioned have the properties of good primary standards. Potassium bichromate, potassium bromate, potassium iodate and iodine are used as primary standards; the other oxidizing agents mentioned must be standardized against suitable reducing agents, which are primary standards, the more important being arsenious oxide, sodium oxalate and pure electrolytic iron. Some of the standard solutions may be prepared directly from primary standards. Sodium arsenite, for example, may be prepared by dissolving pure arsenious oxide in sodium carbonate solution, and converting the excess of the carbonate into sodium bicarbonate. Oxalic

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[1] The iodine is dissolved in a potassium iodide solution, and the active oxidizing agent appears to be the tri-iodide ion, I_3^-.

acid for use as a reducing agent, may be prepared from the primary standard, sodium oxalate. Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$, can not be dried, and oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, can be dried only under special conditions. Certain reducing solutions such as ferrous sulfate are oxidized by atmospheric oxygen and must either be restandardized frequently or protected by a non-oxidizing atmosphere of nitrogen or carbon dioxide.

Equivalent Weights of Oxidizing and Reducing Agents. The equivalent weight of an oxidizing agent is that weight of it which oxidizes one gram atom of hydrogen, under stated conditions. The equivalent weight of a reducing agent is that weight which produces the same reducing action as one gram atom of hydrogen under the conditions stated. Upon examination of the various oxidation-reduction reactions it is immediately recognized that one gram atom of hydrogen, upon oxidation is changed from the elementary state, often indicated by H^0 to a state indicated by H^{+1}, as for example in the process:

$$2Fe^{+++} + 2H \rightleftharpoons 2Fe^{++} + 2H^+$$

or in

$$2H_2 + O_2 \rightleftharpoons 2\overset{2\times+1}{H_2}\overset{-2}{O}.$$

In these reactions we identify the following changes in state of oxidation, which may be represented by Roman numerals:

$$Fe^{III} \rightleftharpoons Fe^{II};\ H^0 \rightleftharpoons H^I$$

$$O^0 \rightleftharpoons O^{-II};\ \text{and again } H^0 \rightleftharpoons H^I.$$

In every case the molecule or ion which is identified as an oxidizing agent undergoes a change that brings the group as a whole, or one of its parts, to a lower state of oxidation. It is true that in some complicated cases some part of a molecule may be oxidized at the expense of another part of the same molecule; in a case of this kind, the average change per molecule or ion may be readily deduced. The reducing agent is simultaneously oxidized, so that the average change per molecule of the reductant is from a lower to a higher state of oxidation.

The equivalent weight of an oxidizing or a reducing agent may therefore be interpreted as: Molecular weight of the substance divided by the total change in state of oxidation. For example, an acidified solution of ferric sulfate may be reduced by hydrogen:

$Fe_2(SO_4)_3 + H_2 = 2FeSO_4 + H_2SO_4$, from which it is evident that $Fe_2(SO_4)_3$ is equivalent to 2 g. atoms of hydrogen. Hence $\frac{\text{Mol. wt. of } Fe_2(SO_4)_3}{2}$ is the equivalent of ferric sulfate in this case.

Oxidation Number. The number representing the change in state of oxidation is frequently derived by assigning a number to some central atom or atoms in a molecule before and after the change has occurred. The number representing the assigned state of oxidation is called an oxidation number. For example in $K_2Cr_2O_7$ potassium is taken as having a number of plus 1 and oxygen of − 2. Then the number of atoms times the oxidation number is written above the formula:

$$\overset{+2}{K_2}\quad\overset{+12}{Cr_2}\quad\overset{-14}{O_7}.$$

Under conditions where the bichromate is reduced to chromic sulfate, $\overset{2\times 3=+6}{Cr_2}\ \overset{-6}{(SO_4)_3}$, it is evident that the change in oxidation number in this case is from 12 to 6, and that the equivalent weight of potassium bichromate is:

$$\frac{K_2Cr_2O_7}{6} = \frac{294.21}{6} = 49.035 \text{ g.}$$

Such changes in state of oxidation are referred to as changes in oxidation number or changes in polarity. For one who is familiar with the "ion-electron method" of considering oxidation-reduction reactions, the changes in oxidation number are identified as the number of electrons necessary to balance a suitable partial reaction. For example, for bichromate ion the partial reaction may be formulated: $Cr_2O_7^{=} + 14H^+ + 6e = 2Cr^{+++} + 7H_2O$. This expression indicates that six electrons (e) are involved in the reduction of bichromate ion to yield two chromic ions.

When an oxalate is oxidized the carbon is evolved as carbon dioxide. For example: $\overset{+2}{Na_2}\overset{+6}{C_2}\overset{-8}{O_4} \rightarrow \overset{2(+4)}{2CO_2}$. The number assigned to two carbon atoms increases from +6 to +8; in other words the equivalent weight of sodium oxalate as a reducing agent is one-half of its molecular weight, or $\frac{134.014}{2}$.

In the oxidation of sodium thiosulfate, the product is sodium tetrathionate in the conventional applications of this reductant in volumetric analysis:

$$\overset{2(+2\ +4\ -6)}{2(Na_2S_2O_3)} \text{ yield } \overset{+2\ +10\ -12}{Na_2S_4O_6},$$

the oxidation number being +4 for the two atoms of sulfur in sodium thiosulfate, or +8 for four sulfur atoms in two molecules of the compound. In the product a number of +10 is associated with four sulfur atoms. The change in oxidation number is thus 2 per 2 molecules of sodium thiosulfate. The equivalent weight is therefore equal to $\frac{\text{Mol. wt. of } Na_2S_2O_3}{1}$ or $\frac{\text{Mol. wt. } Na_2S_2O_3 \cdot 5H_2O}{1}$ for the commercial crystallized salt.

The equivalent weight of a substance in oxidation-reduction reactions is not necessarily the same for all conditions. Potassium permanganate, for example, in the majority of its applications in 1-2 *N* acid solutions undergoes a change from $\overset{+1+7-8}{KMnO_4}$ to manganous salt, e.g., $\overset{+2\ -2}{MnSO_4}$, a change in oxidation number of five. In neutral, alkaline or feebly acid solutions the product is MnO_2, the change being 3,(+ 7 to + 4). Other less important cases involve the reduction of permanganate to manganate ($KMnO_4$ to K_2MnO_4 in alkaline solution with barium ion present), or to a trivalent salt in the special case of solutions containing fluoride. Hence the equivalent weight may commonly be either ⅕ or ⅓ of the molecular weight, and less commonly either the molecular weight, or ¼ of the molecular weight respectively in the last two processes.

The Balancing of Oxidation-Reduction Equations. The changes in oxidation number must be known for the system: Oxidizing agent and the product to which it is reduced, and for the system: Reducing agent and the product to which it is oxidized. On the basis of electrochemical theory (pp. 204-215) a reasonable prediction may be made as to the products in an unfamiliar case, if the effect of acidity and possible complex-formations can be anticipated. The final decision is most safely and surely found by qualitative and quantitative experiments. In Table XIV, pp. 208-209, is given a summary of the available facts about many important oxidation-reduction systems, together with the characteristic changes in oxidation number and with ion-electron partial equations. The oxidation-reduction systems in this table are arranged according to electrochemical and chemical evidence in order with the more powerful oxidants at the beginning of the table, and the more powerful reductant systems at the end.

When the changes in oxidation number are known, the simplest possible equation can be set down by taking the proper number of molecules of the oxidant and the reductant to give the lowest common multiple of the two changes in oxidation number. To express it as simply as possible, the change in oxidation number of the oxidizing agent gives the number of molecules of the reducing agent required and vice versa. For example, if the change in oxidation number for the permanganate-manganous system is 5, as has been indicated, and that for the oxalate-carbon dioxide system is 2, the lowest common multiple is 10, and the fundamental change will involve the interaction of $2KMnO_4$ and $5H_2C_2O_4$. Sulfuric acid must be present in liberal excess over any requirement of the reaction itself in order to prevent an undesirable side reaction between manganous ion and permanganate ion. The equation may therefore be balanced by taking any convenient number of molecules of sulfuric acid to give reasonable products:

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

A molecular equation is of course arbitrary for a reaction that occurs in dilute solution, since the products are ions. Equations of this arbitrary nature are very useful in understanding the fundamental stoichiometry of a process.

If the ion-electron method is used, the process for the case that has just been discussed will consist in considering the partial reactions for the two systems, so written that the number of electrons expressed for each partial reaction is that of the change in oxidation number for the process:

$$(1)\quad MnO_4^- + 8H^+ + 5e = Mn^{++} + 4H_2O$$

$$(2)\quad C_2O_4^= = 2CO_2 + 2e.$$

The lowest common multiple is 10 electrons, and equation (1) is multiplied by 2, and equation (2) by 5, and the expressions are added, canceling out the electrons:

$$\begin{array}{r}
2MnO_4^- + 16H^+ + 10e = 2Mn^{++} + 8H_2O \\
5C_2O_4^= = 10CO_2 + 10e \\
\hline
2MnO_4^- + 16H^+ + 5C_2O_4^= = 10CO_2 + 2Mn^{++} + 8H_2O.
\end{array}$$

If hydrogen ion and water, or hydroxyl ion and water occur on both sides of an equation obtained by addition in this manner, the final equation is simplified to show each of these substances on one side of the equation. Illustration:

Oxidation of arsenious acid by potassium bichromate:

$$\begin{array}{ll}
(1) & Cr_2O_7^= + 14H^+ + 6e = 2Cr^{+++} + 7H_2O \\
(2) & 3HAsO_2 + 6H_2O = 3H_3AsO_4 + 6H^+ + 6e \\
\hline
 & Cr_2O_7^= + 3HAsO_2 + 8H^+ = 3H_3AsO_4 + 2Cr^{+++} + H_2O.
\end{array}$$

If the partial reactions that are given in a table such as that on pp. 208-209, are based upon detailed electrochemical experiments including definite experimental variations in acidity, one is able to estimate the proper acidity or pH range for a given reaction. Some detailed illustrations are discussed on pages 211-214.

OXIDATION-REDUCTION INDICATORS

Oxidation-reduction indicators change color over a limited range of oxidation potential in much the same way that acid-alkali indicators change color over a narrow range of pH. Such indicators may be used to show the oxidation-reduction intensity of a solution by noting the color. This use, which is analogous to the colorimetric measurement of pH, is rarely encountered except in biochemical studies. In analytical chemistry the chief use of such indicators is at present in connection with oxidation-reduction titrations. The transition ranges of many oxidation-reduction indicators vary systematically with changes in pH.

The Oxidizing or Reducing Agent May Serve as its Own Indicator. If the reagent undergoes a suitable change in color upon oxidation or reduction, the first drop (0.05 ml. or less) in excess of the amount that is necessary to complete a given reaction in a titration will be sufficient to give a perceptible color change. Potassium permanganate is one of the most valuable oxidants for general purposes because of its self-indicating property. As long as the standard permanganate that is being added to a solution is being reduced, the color of the permanganate ion rapidly disappears. As soon as all the reducing agent has been oxidized, a single drop of the standard permanganate solution imparts a faint pinkish or purplish tint to the solution, even though the volume may be several hundred milliliters. If the solution is already highly colored, as for example by chromic ions, the detection of the end-point in this fashion may become difficult or impossible.

The color of iodine, or of ceric sulfate, has been used in the same manner as that of the permanganate ion to indicate end-points in titration with these reagents. Owing to the rather feeble coloring power of these substances, other means of indicating the end-points are generally preferred.

This method of indicating the end-point has the defect that the true equivalence-point is reached before the end-point. At the latter point a visible excess of the reagent is present. Unless conditions are standardized, especially with respect to total volume and background of foreign colored material, the same tint taken as the end-point will be a variable distance beyond the equivalence-point, depending upon the total volume of solution, etc. If a high degree of accuracy is essential one may either use a different method of finding the end-point, or may find by a blank experiment the amount of the reagent that was necessary to produce the visual indication.

Internal Oxidation-Reduction Indicators. (a) *Reversible Systems.* There are many inorganic and organic oxidation-reduction systems that undergo reversible oxidation-reduction changes at various levels on the electrochemical oxidation-reduction scale (see p. 201). At the equivalence-point of an oxidation-reduction titration there is an abrupt change of the solution through intermediate levels of oxidation-reduction intensity. The ideal indicator system is one which changes color in a very short range symmetrically distributed about the level that is calculated or determined for the theoretical equivalence-point. The levels are most conveniently expressed in volts relative to that of the hydrogen-hydrogen ion system at 1 *N* hydrogen-ion concentration taken as zero. At the end-points of various oxidation-reduction titrations the addition of a single drop of 0.05 *N* oxidant or reductant will produce a change of several hundredths or even tenths of a volt. Any indicator that changes sharply within this range may serve, although one changing at the level characteristic of the equivalence-point is the most suitable.

A familiar oxidation-reduction system among those in the inorganic field is the iodine-iodide system, either alone or with starch added. If a little of this mixture containing starch is added, for example, to a stannous solution, the blue iodine starch complex is decolorized. Now as the stannous solution is titrated with bichromate, or ceric sulfate, or other powerful oxidant, the blue color reappears and persists as soon as all of the stannous ion has been oxidized. The iodine-iodide system is approximately midway between the characteristic levels of the stannous-stannic system and the bichromate-chromic system.

Another inorganic system that is useful for indication is the iodine-iodine monochloride system in solutions that contain high concentrations of hydrochloric acid (3-6 *N*). At the end of the oxidation of various reducing agents, e.g., iodide, arsenite, etc., with powerful oxidants ($KMnO_4$; $Ce(SO_4)_2$; $K_2Cr_2O_7$; KIO_3) the free iodine which is liberated in intermediate stages of the reaction from iodine monochloride, added as a catalyst and an indicator, is sharply decolorized at the end-point. The color change is best seen in a layer of chloroform or carbon tetrachloride with which the solution is shaken after each addition of reagent near the end-point. In this layer the purple of the iodine changes to the faintly yellow color of iodine monochloride.

Reversible Organic Systems. At a given acidity an organic substance may be capable of being oxidized or reduced with marked change in color. The change occurs at a level which varies in a systematic manner with the acidity of the solution, and hence a proper choice may be made for reactions that proceed in a known range of acid concentration. In the range between powerful reducing agents such as titanous solutions and the moderate to strong oxidizing agents, ferric ion, arsenate, etc., up to permanganate or ceric ion there are many substances that are sharply decolorized or changed by a single drop of 0.1 *N* titanous solution added in the end-point region. Methylene blue, many of the indophenols and other substances are available in this region.[1] General practical importance lies in indicators that operate at levels that are of interest in titrations that may be made without excluding air. Some of the indicators that are useful in the upper regions of the oxidation-reduction scale will now be mentioned.

Orthophenanthroline-Ferrous Ion Indicator, $Fe(C_{12}H_8N_2)_3^{++}$. The red complex ferrous ion is oxidized to the pale blue complex ferric ion, at a high level on the oxidation-reduction scale (about 1.14 volts).

$$\underset{\text{deep red}}{Fe(C_{12}H_8N_2)_3} \rightleftharpoons \underset{\text{pale blue}}{Fe(C_{12}H_8N_2)_3} + e.$$

This complex was discovered by Blau[2] and introduced into volumetric analysis by Walden, Hammett and Chapman.[3] The indicator has been employed in the reaction between ferrous iron and bichromate solution. The color change is sluggish when titrating with standard bichromate solution, but more rapid in the reverse titration. The chief applications of the indicator are in titrations of: Fe^{II}, $C_2O_4^{=}$, As^{III}, Sb^{III}, $Fe(CN)_6^{\equiv}$, Tl^{I}, U^{IV} or H_2O_2 with ceric solutions, or for the titration of ceric solutions with Fe^{II}, NO_2^-, H_2O_2, etc.[4] In the latter cases the indicator is added after the major part of the ceric ion has been reduced. Gleu[5] found that a few drops of 0.01 *M* OsO_4 solution catalyzes oxidation of As^{III} by ceric or permanganate ions; the titrations may then be made at room

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[1] For systematic studies of the behavior of oxidation-reduction systems, especially organic ones at the lower oxidation-reduction levels, see W. M. Clark and collaborators, "Studies on Oxidation-Reduction," I-X, Bulletin No. 151, U. S. Hygienic Laboratory, Public Health Service. Further studies appear in U. S. Public Health Reports, 1928 and later. A detailed summary of oxidation-reduction indicators for volumetric analysis is given in Newer Methods of Volumetric Analysis, Chapter by E. Brennecke (transl. by R. E. Oesper), D. Van Nostrand Co.

[2] Blau, Monatsh. **19**, 647 (1898).

[3] G. H. Walden, Jr., L. P. Hammett and R. P. Chapman, J. Am. Chem. Soc. **53**, 3908 (1931); **55**, 2649 (1933); G. H. Walden, Jr., L. P. Hammett and S. M. Edmonds, J. Am. Chem. Soc. **56**, 57, 350 (1934).

[4] H. H. Willard and P. Young, J. Am. Chem. Soc., **55**, 3260 (1933).

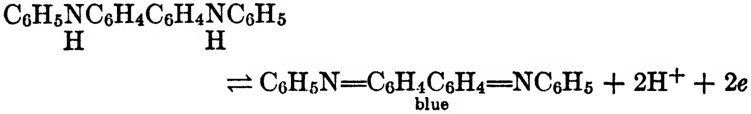
[5] K. Gleu, Z. anal. Chem. **95**, 305 (1933).

temperature, which is important, since the indicator is decomposed in a few minutes in hot solutions. The indicator system is remarkably stable toward high concentrations of Cd^{++}, Zn^{++}, Co^{++}, Ni^{++} and Cu^{++}; rather high concentrations of mineral acids have only slow destructive action upon the indicator at room temperature. The nitro-derivative of the indicator changes color at an even higher level (1.25 v.) than the unmodified compound.

Diphenylbenzidine; Diphenylamine; Sodium Diphenylamine Sulfonate. Diphenylbenzidine, or substituted derivatives, is formed as an oxidation product of diphenylamine or the sulfonates:

$$2(C_6H_5)_2NH + O = C_6H_5\underset{H}{N}C_6H_4C_6H_4\underset{H}{N}C_6H_5 + H_2O.$$

Diphenylbenzidine is further oxidized to a deep blue compound which is the principal indicating substance:



$$C_6H_5\underset{H}{N}C_6H_4C_6H_4\underset{H}{N}C_6H_5 \rightleftharpoons \underset{\text{blue}}{C_6H_5N{=}C_6H_4C_6H_4{=}NC_6H_5} + 2H^+ + 2e$$

On reduction this forms a green addition product so that the color change in this direction is from blue to green. Hence if diphenylamine or its derivatives are used the first part of the action is an irreversible oxidation to the diphenyl benzidine system. The latter upon mild oxidation undergoes a nearly reversible change, but upon drastic oxidation the indicating system is destroyed. Knop[1] introduced diphenylamine as an indicator in the titration of ferrous iron with potassium bichromate. The sulfonic acid derivative[2] has advantages over the parent substance in stability and brilliance of color. Tungsten does not interfere with its use as it does with diphenylamine.[3] Diphenylbenzidine solutions are rather unstable; when the parent

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[1] J. Knop, J. Am. Chem. Soc. **46**, 263 (1924). See E. Brennecke, Newer Methods of Volumetric Analysis, Chapter VI, Transl. by R. E. Oesper, D. Van Nostrand Co., for a comprehensive review of oxidation-reduction indicators.

[2] L. A. Sarver and I. M. Kolthoff, J. Am. Chem. Soc. **53**, 2902, 2906 (1931).

[3] H. H. Willard and P. Young, Ind. Eng. Chem. Analyt. Ed., **4**, 187 (1932).

substances (diphenylamine, etc.) are used corrections must be applied to account for the irreversible part of the oxidation. With 0.1 N solutions one drop (0.05 ml.) of oxidizing agent is required for the color change when 2-3 drops of 1 per cent indicator solution are used. All of these systems lie rather close to the ferric-ferrous level (0.75 v.) and hence phosphoric acid is added to bind the ferric ions and thus bring the ferrous-ferric system below the level of the indicator system.

The introduction of a carboxyl group into diphenylamine in the ortho position to form phenylanthranilic acid raises the potential at which the indicator changes color to 1.08 volts.[1]

Triphenylmethane Indicators. Many compounds of this type undergo a reversible oxidation-reduction color change at 0.99-1.09 v. in 1-2 N acid solutions. Erio green, erio glaucine and similar substances are serviceable in titrations of ferrocyanide, ferrous ion, etc., with potassium permanganate or with ceric sulfate. The indicators are of pale greenish yellow color in acidified solutions of reducing substances and change sharply to rose when the reductant has been oxidized.

(b) **Irreversible Indicators.** In certain cases, notably in titrations with potassium bromate, a few drops of 0.1 per cent methyl orange or other organic dye is added. At the end-point the first slight excess of the bromate reacts with bromide already present to yield free bromine which bleaches the indicator. A correction may be determined, or the solution may be standardized under the same conditions.

Electrochemical Indication. The changes in electromotive force of a cell made up of: A platinum wire : solution titrated : reference half-cell serves to give an indication of the course of all of the oxidation-reduction reactions that one is apt to encounter in volumetric analysis. Occasionally instances of electrode poisoning or irreversible behavior may make it impossible to obtain satisfactory indication by this technique, but it is the closest approach to a universal oxidation-reduction indicating method that is now available.[2]

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[1] W. S. Syrokomsky and V. V. Stiepin, J. Am. Chem. Soc. **58**, 928 (1936).

[2] For details of apparatus and applications see I. M. Kolthoff and N. H. Furman, Potentiometric Titrations, 2nd Ed., J. Wiley & Sons, Inc., New York, 1931.

TABLE XII. APPROXIMATE POTENTIALS (E_H) AT WHICH VARIOUS OXIDATION-REDUCTION INDICATORS CHANGE COLOR IN SOLUTIONS 1 N IN ACID

Indicator	E_H at Color Change	Color of the Indicator	
		Oxidized Form	Reduced Form
Nitro-o-phenanthroline ferrous sulfate (Nitro-ferroin)	1.25	Blue	Intense Red
O-Phenanthroline ferrous sulfate (Ferroin)	1.14	Blue	Intense Red
Phenylanthranilic acid	1.08	Purplish red	Yellow
Triphenyl methane dyes (Erio green; Erio glaucine, etc.)	0.99–1.09	Rose	Greenish yellow
Diphenylamine; diphenylamine sulfonic acid; diphenylbenzidine	0.76–0.88	Blue	Green
Indophenols	0.6		
Starch iodide (Iodine-KI-Starch)	0.535	Blue	Colorless
Methylene Blue	0.52	Blue	Colorless
Indigo sulfonates	0.26–0.38	Blue	Colorless

External Indicators. In a few cases no satisfactory internal indicator has been found. In these instances a number of drops of a suitable indicating solution is placed on a white tile, or else a special test paper treated with the indicator solution is prepared. The end-point is found by removing and placing in contact with the indicator a small drop of the solution titrated after each drop of the standard volumetric reagent is added near the end of the titration. In the titration of zinc with standard potassium ferrocyanide solution a uranyl salt is used as an external indicator. In the titration of lead with molybdate in acetate solution, tannic acid or a solution of pyrogallol in chloroform is used as an indicator for the presence of molybdate ion.

Oxidations and Reductions Prior to Titrations. In the processes of decomposition and solution of various substances in the course of analyses substances may be obtained in more than one state of oxidation, e.g., ferrous and ferric; vanadyl salts and vanadates (V^{IV} and V^{V}); arsenites and arsenates, etc. Prior to a titration, the substances to be determined are normally subjected to one of two procedures: (1) Complete oxidation of all substances present, or selective oxidation of individual substances by a suitable oxidizing agent. A standard solution containing a reducing agent is then used in the titration. (2) The solution is subjected to complete or to selective reducing action before it is titrated with an oxidizing agent.

In either of the foregoing methods of treatment it is necessary to remove or destroy the excess of oxidizing or reducing agent prior to the titration. Of the powerful oxidizing agents sodium bismuthate, potassium or ammonium persulfate, hydrogen peroxide and potassium permanganate are frequently used. The excess of sodium bismuthate is removed by filtration. The persulfates and hydrogen peroxide are destroyed by boiling, with silver ion as catalyst if necessary. Potassium permanganate is destroyed in one of several ways: by adding hydrochloric acid and boiling, by reduction to MnO_2 followed by filtration, or by adding an azide (NaN_3) and boiling to destroy the excess of the latter. Prior oxidation is very frequently employed in the analysis of steels and ferroalloys for manganese, chromium and vanadium. Numerous selective procedures are available (cf. Iron and Steel, bibliography, Appendix).

The second general method, prior reduction, is very frequently used in the analysis of various substances that contain iron in association with titanium, molybdenum, etc. Table XIII, shows the extent to which various elements are reduced by the reducing agents that are most frequently used.

It will be observed that iron is in all cases reduced to the bivalent stage, whereas other elements, notably Cr, V and Mo are reduced sharply from the highest to the next stage or to a lower one depending upon the specific nature of the reducing agent and the acidity. It is therefore possible to reduce, for example, one aliquot portion of a solution containing molybdenum and iron to Fe^{II} and Mo^{V}; a second aliquot may be reduced to Fe^{II} and Mo^{III}. The difference between the amounts of an oxidizing agent that are required to reoxidize the substances to Fe^{III} and Mo^{VI} in the two cases gives a measure of the amount of molybdenum present. A study of the table will serve to indicate a number of other "differential" reduction and titration

Table XIII. Reducing Action of Various Reductants upon Ferric Iron and Substances Commonly Associated with It

Reducing Agent	Fe^{III} Reduced to	Ti^{IV} Reduced to	V^{V} Reduced to	Cr^{VI} Reduced to	Mo^{VI} Reduced to
1. An active metal (Zn, Al, Cd) plus excess of acid	Fe^{II}	Ti^{III}	V^{III}, V^{II}	Cr^{III}, Cr^{II}	Mo^{III}
2. Amalgams					
Zinc.........	Fe^{II}	Ti^{III}	V^{II}	Cr^{II}	Mo^{III}
Bismuth.....	Fe^{II}	Ti^{III}(*a*)	V^{IV}		(*b*) Mo^{V} or Mo^{III}
Lead........	Fe^{II}	Ti^{III}	V^{II}		Mo^{III}
3. Stannous Chloride in HCl solution	Fe^{II}	Ti^{III} (partial)	V^{II}, V^{III} V^{IV}	Cr^{III}	(*b*) Mo^{V}, Mo^{III}
4. Silver (the substance to be reduced in HCl solution)	Fe^{II}	Not reduced in 1 *N* HCl Sol'n	V^{IV}, V^{III}	Cr^{III}	(*b*) Mo^{V}
5. Mercury, with chloride ion in the solution	Fe^{II}	Not reduced	V^{IV}(*b*)	Cr^{III}	(*b*) Mo^{V}
6. Hydrogen Sulfide	Fe^{II}	Not reduced	V^{IV}	Cr^{III}	Precipitated
7. Sulfur dioxide...	Fe^{II}	Not reduced	V^{IV}	Cr^{III}	Partial

Notes. Air must be excluded from solutions in which it is desired to titrate Ti^{III}, V^{II}, V^{III}, Cr^{II} or Mo^{III}.

(*a*) Complete at high acidity, see Fig. 50.

(*b*) In these cases the reduction proceeds to a greater extent at higher acidities. At low acidities the reduction to V^{IV} or Mo^{V} is quantitative; further reduction occurs at greater acidities. See Fig. 49.

References to Table XIII. Details regarding reduction by various amalgams are to be found in numerous papers by N. Kano, T. Nakazono, K. Someya and others in the period from 1921-1928. K. Someya, Sci. Report Tohoku Imperial University, Ser. I., Vol. **14,** 47 (1925) (gives references to earlier investigations). Z. anorg. allgem. Chem., **145,** 168 (1925); **148,** 58 (1925); **152,** 368 (1926); **152,** 382 (1926); **152,** 386 (1926); **160,** 355 (1927); **160,** 404 (1927); **163,** 208 (1927); **169,** 293 (1928).

Details regarding the silver reductor are given by: G. H. Walden, Jr., L. P. Hammett and S. M. Edmonds, J. Am. Chem. Soc. **56,** 350 (1934); N. Birnbaum and G. H. Walden, Jr., *ibid.* **60,** 64 (1938). N. Birnbaum and S. M. Edmonds, Ind. Eng. Chem. Analyt. Ed., **12,** 155 (1940).

Mercury Reductor: L. W. McCay and W. T. Anderson, Jr., J. Am. Chem. Soc. **43,** 2372 (1921); **44,** 1018 (1922); N. H. Furman and W. M. Murray, Jr., *ibid.* **58,** 1689 (1936); McCay, Ind. Eng. Chem. Analyt. Ed. **5,** 1 (1933).

processes of this general nature. Details regarding the use of various reducing agents are to be found on pp. 224-227.

THE ELECTROCHEMICAL THEORY OF OXIDATION-REDUCTION REACTIONS[1]

The electrochemical series of the elements may be regarded as an oxidation-reduction series that gives an indication of the tendency of one element to reduce the oxidized form of another element: $Zn + Cu^{++} \rightleftharpoons Cu + Zn^{++}$. The driving force of the reaction and the state of equilibrium is recorded in the standard potentials for the two electrodes: Zn/Zn^{++} and Cu/Cu^{++}. All other systems that show reversible electrode behavior may be

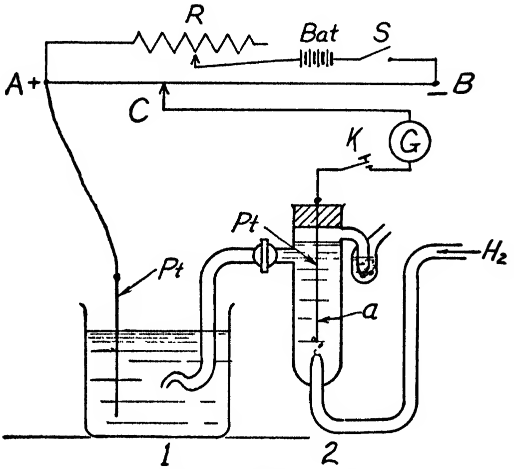

FIG. 44. Apparatus for Measuring E.M.F. The uniform wire *AB* has a definite fall of potential from *A* to *B* per unit of length. The total value, *A-B,* is adjusted by the battery, Bat, Resistance, *R,* with switch, *S,* closed, and a standard (not shown) which is introduced between *A* and *K*. *C* is a sliding contact, *K* a tapping key and *G* a galvanometer. Beaker *1* contains the oxidation-reduction system, in this case a solution 1 *M* in both $FeCl_2$ and $FeCl_3$ and HCl. Vessel *2* contains 1 *M* HCl, and upon bubbling hydrogen gas at 1 atmosphere into contact with the platinized platinum wire, *a,* the half-cell, *2,* becomes a standard hydrogen electrode. When a position for *C* is found at which the galvanometer, *G,* shows no deflection when key, *K,* is closed momentarily, the E.M.F. of cell *1-2* is to the E.M.F. *A* to *B* as distance *AC* is to *AB.*

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[1] A further discussion of electrode processes is given in Chapter XIX.

added to the oxidation-reduction potential series. If both the oxidized and reduced forms of the system are soluble ions, e.g., Fe^{+++} and Fe^{++}, the potential is measured with the aid of a platinum wire, which presumably assumes a potential indicative of the equilibrium $Fe^{+++} + e \rightleftharpoons Fe^{++}$, in much the same fashion as a copper wire indicates the equilibrium between $Cu^{++} + 2e \rightleftharpoons Cu$, or a platinum wire coated with platinum black indicates the equilibrium of the process $2H^+ + 2e \rightleftharpoons H_2$ (hydrogen electrode). For any pair of electrodes the tendency of current to pass in the external circuit is measured by a balancing or compensation method as is indicated in Fig. 44. In this figure the cell is set up to measure the tendency of hydrogen at one atmosphere pressure in 1 *M* hydrochloric acid to reduce ferric iron in a mixture 1 *M* in each of the substances: Ferric chloride, ferrous chloride and hydrogen chloride. In cells of this type there is always a liquid junction effect at the point of contact of the two solutions. This effect is in general small and will be neglected for purposes of the present discussion. As a matter of practical convenience a calomel half-cell, Fig. 45, consisting

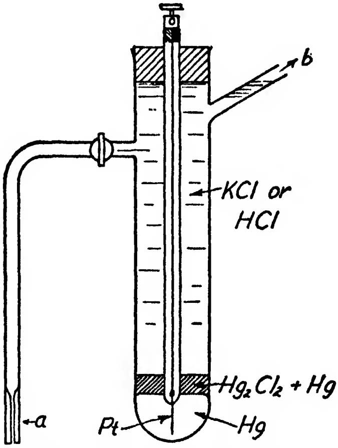

FIG. 45. Calomel Half-Cell. The potential at the interface Hg-Calomel is determined by the concentration of mercurous ions, and the latter concentration is fixed by the common ion effect if the temperature and the concentration of chloride ion are fixed. The standard electrodes are filled with potassium chloride solutions that are either 0.1, 1, 3.5 *M* or saturated; 0.1 or 1 *M* HCl solutions are often used. Each of these six fillings gives a cell of definite value relative to the standard hydrogen electrode.

of mercury, covered with a layer of calomel-mercury mixture and either a potassium or hydrogen chloride solution of known concentration is often used in place of the hydrogen electrode. Any measurement made relative to such half-cells may be referred to the hydrogen electrode since careful measurements have been made for numerous half-cells relative to the standard hydrogen electrode. For example, a given reference electrode has a measured value of 0.246 v. relative to the hydrogen electrode which is given a reference value as zero. An oxidation-reduction system is more positive by 0.504 v. than the reference electrode. The system relative to the hydrogen electrode then has a value of 0.504 plus 0.246 = 0.750 v. relative to the hydrogen standard.

It has been found experimentally that the electrochemical behavior of an oxidation-reduction system as a function of temperature and concentrations of oxidant and reductant may be summed up in the expressions: $\mathrm{Ox} + ne \rightleftharpoons \mathrm{Red}$, and

$$E = E_0 + \frac{0.0001983T}{n} \log \frac{[\mathrm{Ox}]}{[\mathrm{Red}]}$$

E being the E.M.F. in volts relative to the standard hydrogen electrode taken as zero, [Ox] the molar concentration of the oxidant, Ox, and [Red] that of the reductant, n the change in oxidation number, or change in number of electrons, e, per molecule of oxidant, T the absolute temperature and log denotes common logarithms (base (10).[1] E_0 is the value for the system when [Ox] = [Red], both [Ox] and [Red] being at the standard state.[2]

These E_0 values are characteristic constants for each oxidation-reduction system. A number of the E_0 values that are of interest in analytical chemistry are assembled in Table XIV, together with other useful information about the system. If hydrogen ions take part in the electrode reactions, or are necessary to prevent hydrolysis, the values given are for solutions 1 M in hydrogen ion.

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[1] The expression $0.0001983T$ is equal to 0.0591 at 25° C.

[2] The standard state for dissolved substances is strictly an activity of 1 Molal (1 mole per 1000 g. of water). For details as to precise relations in this field see W. M. Latimer, Oxidation Potentials, Chapter I. Prentice-Hall, Inc., New York, 1938.

The oxidation level of ferric-ferrous salt mixtures at constant acidity and constant temperature (25° C.) varies 0.0591 volt for each tenfold change in the ratio of ferrous and ferric ions:

Ratio, $\frac{[Fe^{+++}]}{[Fe^{++}]}$	$\frac{1}{1000}$	$\frac{1}{100}$	$\frac{1}{10}$	$\frac{1}{1}$	$\frac{10}{1}$	$\frac{100}{1}$	$\frac{1000}{1}$
$E_{Fe^{+++}/Fe^{++}}$	0.594	0.653	0.712	0.771	0.830	0.889	0.948

In general the change is $\frac{0.0591}{n}$ per tenfold change in the ratio $\frac{[Ox]}{[Red]}$, where n is the change in oxidation number. The relations for the various systems at constant acidity and temperature may be plotted conveniently as a function of per cent of the system oxidized, as has been done in Fig. 46 for a number of familiar systems.

The Course of Oxidation-Reduction Titrations. The change in oxidation-reduction intensity (E vs. a reference electrode) during a titration is in general that which would be anticipated from an inspection of Fig. 46. For example in the titration of a ferrous solution with a solution of potassium permanganate the graph of E vs. a reference half-cell is given in Fig. 47. In the mid-portions of the titration the ratio $\frac{[Fe^{+++}]}{[Fe^{++}]}$ does not change through many tenfold values, but as the last traces of ferrous iron are oxidized the ratio changes abruptly through several tenfold stages (100/1; 1000/1, etc.) and the oxidation-reduction level rises abruptly to that characteristic of the $[MnO_4^{-}]/[Mn^{++}]$ system. The equivalence-point lies on the vertical portion of the curve at a point which may be calculated from the E_0 values for the two systems.[1] If the equivalence-

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[1] In this case it is $\frac{5E_0 + E'_0}{5+1}$, where E_0 is that for the permanganate system (*or in general for the more powerfully oxidizing system*) and E'_0 is that of the ferric-ferrous system. In general the equivalence-potential E_E for a reaction $aOx_1 + b\text{Red}_2 = a\text{Red}_1 + bOx_2$ is given by:

$$E_E = \frac{bE_0 + aE'_0}{a+b}$$

See Kolthoff and Furman, Potentiometric Titrations, 2nd Ed., p. 45 ff., J. Wiley & Sons, Inc., New York, for further discussion and illustrations.

TABLE XIV. RELATIVE OXIDIZING POWER OF VARIOUS SYSTEMS

In Acid Solution (H) = 1, unless otherwise stated

E_0 (ref. to *N* hyd. Elect. = 0)*	Oxidized Form	Reduced Form	Change in Oxidation Number	Ionic Partial Reaction	Equivalent Weight Showing Relation to Molar Weight
1.67	$KMnO_4$	MnO_2	3	$MnO_4^- + 4H^+ + 3e \rightleftharpoons MnO_2 + 2H_2O$‡	$\frac{KMnO_4}{3}$
1.61	$H_2Ce(NO_3)_6$	Ce^{+++}	1	$Ce(NO_3)_6^= + e \rightleftharpoons Ce^{+++} + 6NO_3^-$	$(NH_4)_2Ce(NO_3)_6$
1.52	$KMnO_4$	$MnSO_4$ or Mn^{++}	5	$MnO_4^- + 8H^+ + 5e \rightleftharpoons Mn^{++} + 4H_2O$	$\frac{KMnO_4}{5}$
1.52	$KBrO_3$	KBr	6	$BrO_3^- + 6H^+ + 6e \rightleftharpoons Br^- + 3\ H_2O$	$\frac{KBrO_3}{6}$
1.44	$Ce(SO_4)_2$	Ce^{+++}	1	$Ce^{++++} + e \rightleftharpoons Ce^{+++}$ †	$Ce(SO_4)_2$
1.36	$K_2Cr_2O_7$	$2Cr^{+++}$	6	$Cr_2O_7^= + 14H^+ + 6e \rightleftharpoons 2Cr^{+++} + 7H_2O$	$\frac{K_2Cr_2O_7}{6}$
1.3583	$\frac{1}{2}Cl_2$	Cl^-	1	$\frac{1}{2}Cl_2 + e \rightleftharpoons Cl^-$	$\frac{1}{2}Cl_2$; Cl^-
1.28	MnO_2	Mn^{++}	2	$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{++} + 2H_2O$	$\frac{MnO_2}{2}$
1.229	$\frac{1}{2}O_2$	$O^=$	2	$\frac{1}{2}O_2 + 2H^+ + 2e \rightleftharpoons H_2O$	$\frac{O}{2}; \frac{O_2}{4}$
1.085	KIO_3	KI	6	$IO_3^- + 6H^+ + 6e \rightleftharpoons I^- + 3H_2O$	$\frac{KIO_3}{6}$
1.0652	$\frac{1}{2}Br_2$	Br^-	1	$\frac{1}{2}Br_2 + e \rightleftharpoons Br^-$	$\frac{1}{2}Br_2$; Br^-
1.000	HVO_3 or H_3VO_4	$VOSO_4$	1	$VO_4H_4^+ + 2H^+ + e \rightleftharpoons VO^{++} + 3H_2O$	HVO_3; V
0.771	Fe^{+++}	Fe^{++}	1	$Fe^{+++} + e \rightleftharpoons Fe^{++}$	Fe; $\frac{1}{2}Fe_2(SO_4)_3$
0.566	$CuCl_2$	$CuCl$	1	$Cu^{++} + 2Cl^- + e \rightleftharpoons CuCl_2^-$	Cu
0.559	H_3AsO_4	$HAsO_2$ or H_3AsO_3	2	$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons HAsO_2 + 2H_2O$	$\frac{H_3AsO_4}{2}; \frac{As_2O_3}{4}$

0.5345	$\frac{1}{2}I_2$ or $\frac{1}{3}I_3^-$	I^-	1	$\frac{1}{2}I_2 + e \rightleftharpoons I^-$	$\frac{1}{2}I_2$; KI
0.36	$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	1	$Fe(CN)_6^{\equiv} + e \rightleftharpoons Fe(CN)_6^{\equiv}$	$K_3Fe(CN)_6$; $K_4Fe(CN)_6$
0.3448	Cu^{++}	Cu	2	$Cu^{++} + 2e \rightleftharpoons Cu$	$\frac{Cu}{2}$
0.33	UO_2^{++}	U^{++++}	2	$UO_2^{++} + 4H^+ + 2e \rightleftharpoons U^{++++} + 2H_2O$	$\frac{U}{2}$; $\frac{UO_2^{++}}{2}$
0.314	VO^{++}	V^{+++}	1	$VO^{++} + 2H^+ + e \rightleftharpoons V^{+++} + 2H_2O$	V; $VOSO_4$
0.15	Sn^{++++}	Sn^{++}	2	$Sn^{++++} + 2e \rightleftharpoons Sn^{++}$	$\frac{Sn^{++}}{2}$; $\frac{SnCl_2}{2}$
0.1	Ti^{++++}	Ti^{+++}	1	$TiO^{++} + 2H^+ + e \rightleftharpoons Ti^{+++} + H_2O$	Ti; $TiCl_3$
0.000 (std.)	H^+	$\frac{1}{2}H_2$	1	$2H^+ + 2e \rightleftharpoons H_2$	H^+; H; $\frac{1}{2}H_2$
−0.136	Sn^{++}	Sn	2	$Sn^{++} + 2e \rightleftharpoons Sn$	$\frac{1}{2}Sn^{++}$; $\frac{1}{2}Sn$
−0.2	V^{+++}	V^{++}	1	$VO^+ + 2H^+ + e \rightleftharpoons V^{++} + H_2O$	VO^+; V^{++}; V
−0.41	Cr^{+++}	Cr^{++}	1	$Cr^{+++} + e \rightleftharpoons Cr^{++}$	Cr^{+++}; $CrCl_2$
−0.7620	Zn^{++}	Zn	2	$Zn^{++} + e \rightleftharpoons Zn$	$\frac{1}{2}Zn$; $\frac{1}{2}ZnCl_2$

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* The numerical values are from Oxidation Potentials, by W. M. Latimer, Copyright 1938 by Prentice-Hall, Inc., New York, and reproduced here with permission. The sign given to the values is that which is observed experimentally relative to a standard hydrogen electrode in a cell Pt Oxid.-Red. System Hydrogen Electrode in a solution 1 *M* in H^+.

† The ceric ions are probably present as $Ce(SO_4)_3^{=}$.

‡ In neutral or alkaline solution.

The table does not include the following common reagents for which approximate E_0 values are given by Latimer (loc. cit.) as follows:

	E_0 Volts		E_0 Volts
Sodium bismuthate (Bi_2O_5 (approx.) → BiO^+)	1.6	Nitric acid ($HNO_3 \rightarrow HNO_2$)	0.94
Ammonium persulfate → sulfate	2.05	Antimonic acid ($Sb_2O_5 \rightarrow SbO^+$)	0.64
Hydrogen peroxide ($H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$)	1.77	Thiosulfate (oxidized to tetrathionate)	0.17
Reduction potential ($O_2 \rightarrow H_2O_2$)	0.682	Sulfite (oxidized to sulfate)	0.20
Nitric acid (conc.) ($HNO_3 \rightarrow NO_2$)	0.81	Sulfide (oxidized to free sulfur)	0.14
Nitrous acid ($HNO_2 \rightarrow NO$)	0.99		

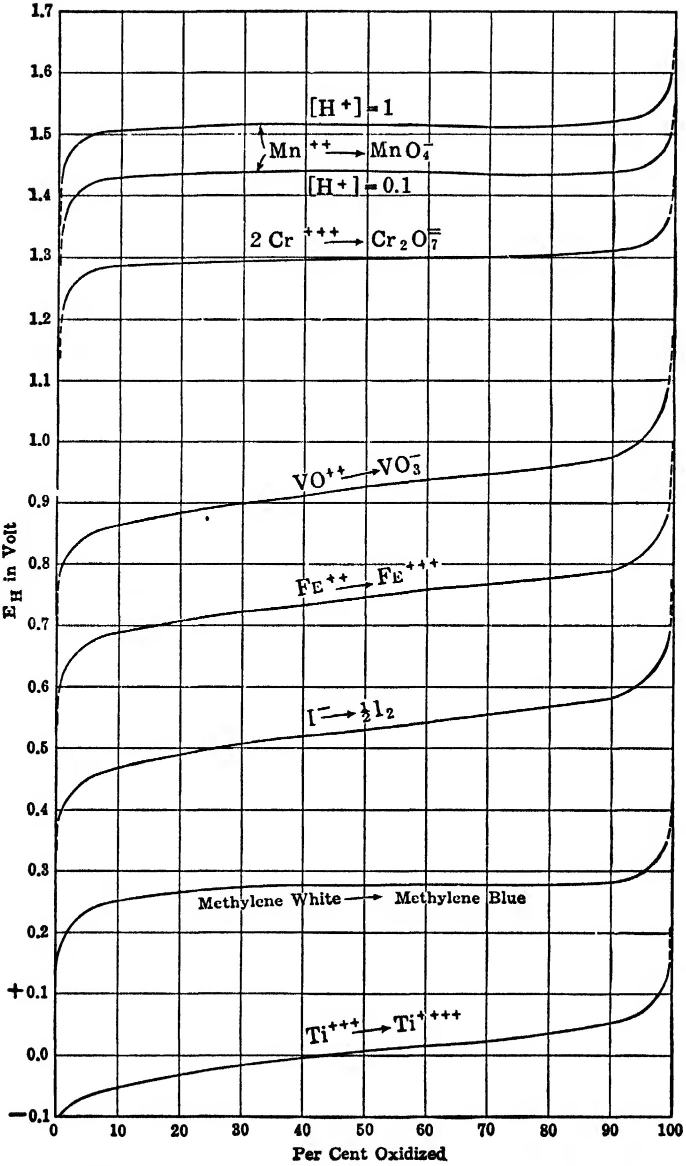

FIG. 46. Oxidation Potential as a Function of the Ratio: [Oxidant] : [Reductant] for various systems.

potential is known an oxidation-reduction indicator that changes color at or very close to the equivalence potential is chosen in those instances where the reagent does not serve as its own indicator.

The Effect of Acidity upon Oxidation-Reduction Titrations Complex-Formation. If hydrogen or hydroxyl ions enter into the electrode reaction, substantially the same treatment that has been given for the simpler cases will apply at any given acidity.

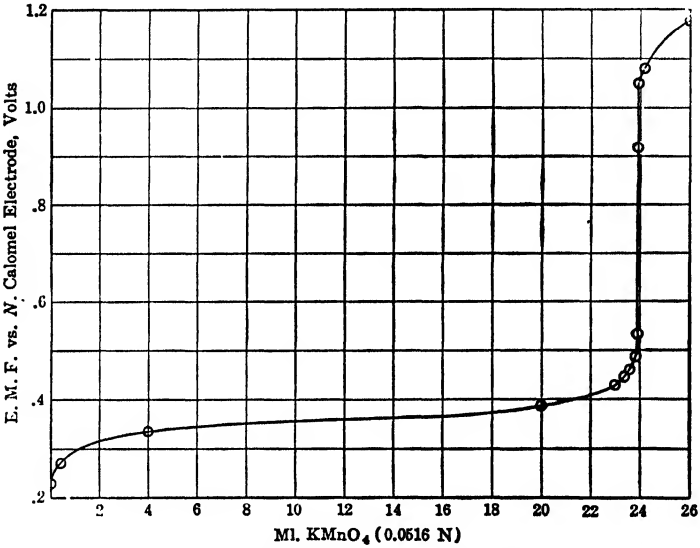

Fig. 47. Graph of Data for Titration of 25 Ml. of 0.0493 *N* Ferrous Sulfate with 0.0516 *N* Potassium Permanganate. The E.M.F. values are relative to an approximately *N* calomel electrode. Referred to the *N* hydrogen electrode each point on the curve would be displaced upward by a constant amount of about 0.3 volt.

If complex formation or very great changes in relative activities of the ions of the reductant and oxidant of a given system are known to occur, these effects are best summarized by plotting the apparent E_0 value for the 1 : 1 mixture of the oxidant and its reduction product at various acidities and at various concentrations of the complex-forming substance.

The system: Arsenate/Arsenite is an important one for analysis; the E value for a 1 : 1 mixture of arsenate and arsenite is shifted very considerably by change of acidity, as might be expected from the following relations:

$$H_3AsO_4 + 2H^+ + 2e \rightleftharpoons HAsO_2 + 2H_2O.$$

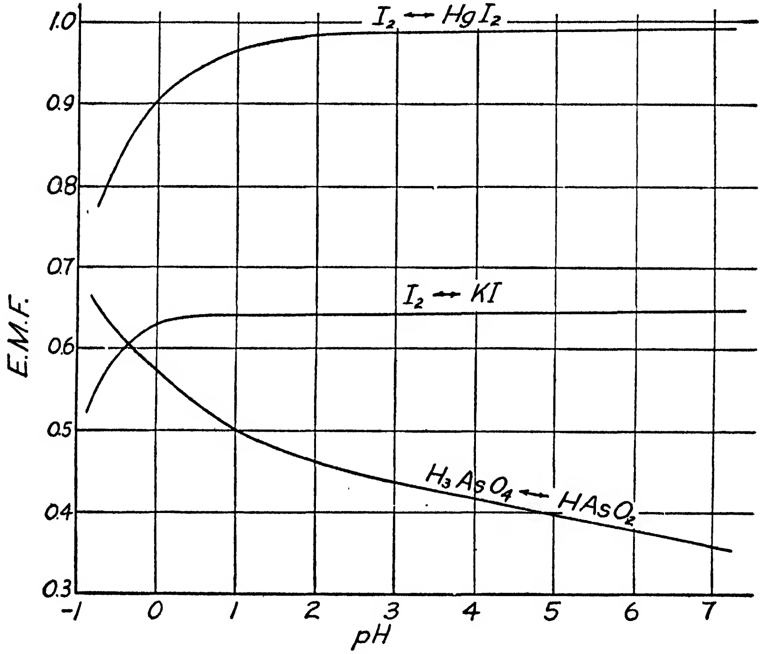

FIG. 48. The Effect of Complex-formation and of Acidity upon Certain Oxidation-Reduction Systems. From 1 *N* acidity ($pH = 0$) to pH 7 acidity has little effect upon the iodine-iodide system, but has a profound effect upon the arsenate-arsenite system. The addition of 2 g. of $HgCl_2$ per 50 ml. of the same solution used in determining the I_2-KI curve lifts the value in each instance to the I_2-HgI_2 level. At acidities greater than 1 *M* the I_2-KI system is affected, presumably by change in the ionization and activity of the ions of the system since the measurements were made on rather dilute systems (0.01 *N* for each reactant).

Regarding the concentration of water as constant, the expression: $E = E_0 + \frac{0.0591}{2} \log \frac{[H_3AsO_4][H^+]^2}{[HAsO_2]}$, applies at 25° C. E_0 is 0.559 v. The electrode equation may be rewritten: $E = 0.559 + \frac{0.0591}{2} \log \frac{[H_3AsO_4]}{[HAsO_2]} + 0.0591 \log [H^+]$ ($\frac{1}{2} \log [H^+]^2 =$

log $[H^+]$). Hence if no other effects occur the effect of changes in pH or $[H^+]$ upon the oxidation-reduction level of the system may be predicted. The iodine-iodide system is one that is only slightly affected by acidity in the pH range 0 to 7. Hence the well-known fact that iodine oxidizes arsenite quantitatively in a bicarbonate medium may be correlated with the fact that in 4-6 N acid arsenate oxidizes iodide practically completely to free iodine, the dominant factor being the effect of acidity upon the level of the arsenate-arsenite system.

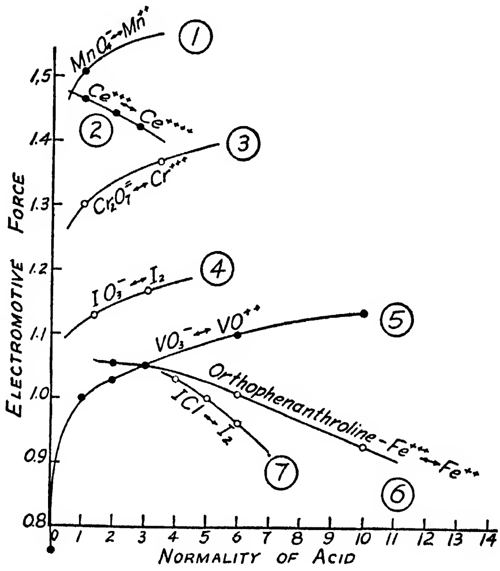

FIG. 49. The Effect of Acidity upon Oxidation-Reduction Levels. The values are for equivalent mixtures of the oxidant and reductant at various concentrations of the acid. The values for systems *1*, *2*, *5* and *6* are for sulfuric acid, the others for hydrochloric. For systems *1* and *3* the values are approximate, since the systems do not establish a measurable equilibrium.

The level of the iodine-iodide system is considerably shifted by having mercuric chloride present in the solution that is titrated. The iodide is then bound either as undissociated mercuric iodide or as a complex anion, and the iodine system now lies so far above that of the arsenate-arsenite system that iodine may be used to titrate arsenite in 1-2 M HCl solution.[1]

When actual data are available as to the effect of acidity upon the levels of 1 : 1 mixtures of various oxidizing agents and their reduction products the data may be plotted and the systems of interest may be compared. A decision may then be made as to whether a given reaction might proceed, and as to the probability of finding an indicator.

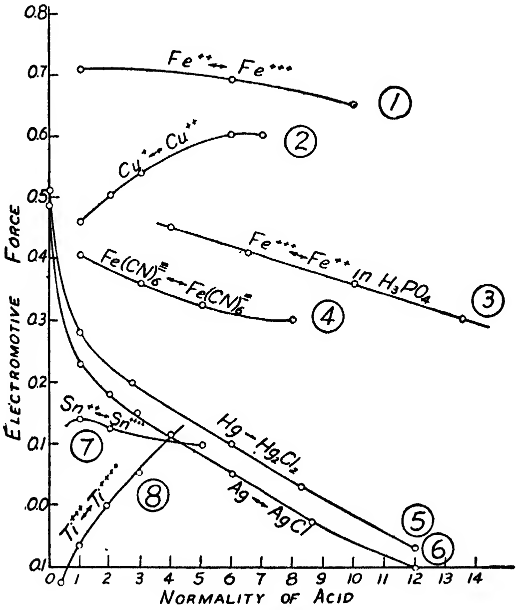

FIG. 50. The Effect of Acidity upon Oxidation-Reduction Levels. (Cont.) (See Fig. 49.) System (1) was measured in sulfuric acid; in hydrochloric acid the level is lower, running from 0.7 volt at 1 N down to 0.6 volt at 8 N. The same system in phosphoric acid lies very much lower owing to the complex formation (formation of non-ionized complexes with ferric ions) (curve 3). The other systems were measured in hydrochloric acid solutions.

Illustration: In the oxidation of arsenite by iodine with mercuric chloride present, the difference in apparent E_0 values for

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[1] The details of this latter case were pointed out by N. H. Furman and C. O. Miller, J. Am. Chem. Soc. **59**, 153 (1937). The graphs in Fig. 48 are plotted from this work.

the two systems in 1 *M* hydrochloric acid is approximately 0.34 volt (Fig. 48). This indicates a completeness of oxidation to within 1 part per 1000 at the end-point. It was found experimentally that the reaction was quantitative within the error of measurement at low acidities, but not in 4 *M* acid concentration where the difference in the apparent E_0 values is insufficient for complete reaction.

The observed variations of the apparent E_0 values of a number of important systems with acidity are plotted in Figs. 49 and 50.[1]

The electrochemical theory gives an approximation of the equilibrium conditions, but yields no information regarding the rate at which equilibrium is established. For example, arsenites should be easily and completely oxidized at room temperature by an equivalent amount of potassium permanganate or of ceric sulfate; in both cases a catalyst must be added in order to make the reaction rate suitable for titrations. The permanganate reaction is catalyzed by as little as 0.05 ml. of 0.0025 *M* solution of any iodine compound; the ceric reaction is catalyzed by a trace of osmium tetroxide; both reactions are catalyzed by iodine monochloride at high acidities. Hundreds of instances of catalytic action in processes of this kind have been noted.[2]

EQUILIBRIUM CONSTANTS; COMPLETENESS OF REACTION AT THE EQUIVALENCE-POINT; EQUIVALENCE-POTENTIAL

A complete and detailed treatment of these topics is beyond the scope of this text.[3] The kinds of information that may be obtained from a table of standard potentials are extensively covered in treatises on physical chemistry.

For a volumetric reaction of the type:

$$\mathrm{Ox}_1 + \mathrm{Red}_2 \rightleftharpoons \mathrm{Red}_1 + \mathrm{Ox}_2,$$

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[1] These data were assembled from the literature by Dr. W. M. Murray, Jr.

[2] G. Woker, Die Katalyse. Die Rolle der Katalyse in der analytischen Chemie. Vols. XI, XII, Die Chemische Analyse, edited by W. Böttger. F. Enke, Stuttgart.

[3] See Kolthoff and Furman, Potentiometric Titrations, 2nd Ed., 1931. John Wiley & Sons, Inc., New York, for a more extended treatment.

where Ox_1 and Red_1 refer to the oxidizing agent and its product of reaction and Ox_2, Red_2 to the reducing agent and its product of reaction, the equilibrium constant is:

$$K = \frac{[Red_1]\,[Ox_2]}{[Ox_1]\,[Red_2]}.$$

Example.[1] $Ce^{++++} + Fe^{++} \rightleftharpoons Fe^{+++} + Ce^{+++}$.

At equilibrium it is assumed that the ceric-cerous and the ferrous-ferric systems are not only at the same chemical potential but also at the same electrical potential. The two electrode expressions are equated:

$$E'_0 + \frac{0.0591}{n} \log \frac{[Ox_1]}{[Red_1]} = E''_0 + \frac{0.0591}{n} \log \frac{[Ox_2]}{[Red_2]}, \text{ at } 25° \text{ C.},$$

from which

$$E'_0 - E''_0 = \frac{0.0591}{n} \left(\log \frac{[Ox_2]}{[Red_2]} - \log \frac{[Ox_1]}{[Red_1]} \right) =$$

$$\frac{0.0591}{n} \log \frac{[Red_1]\;[Ox_2]}{[Ox_1]\;[Red_2]} = \frac{0.0591}{n} \log K.$$

$$\log K = \frac{n}{0.0591} (E'_0 - E''_0)$$

The constant may be calculated for nitrato-cerate and ferrous solution, taking 1.61 for the former system and 0.771 v. for the latter system:

$$\log K = \frac{1}{0.0591} (1.61 - 0.771) = 14.2 \text{ or } K = 10^{14.2},$$

indicating a reaction that should proceed far to the right.

The calculation of the concentrations at equilibrium is of the simplest possible nature when equivalent quantities of the two reactants have been brought together as is always the case at the equivalence-point. If *a* moles of ceric sulfate are added to the

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[1] It is probable that ceric ions exist principally as complex anions of the type $Ce(ClO_4)_6^{=}$, $Ce(SO_4)_3^{=}$, etc., as has been proposed by G. F. Smith and C. A. Getz, Ind. Eng. Chem. Analyt. Ed. **10**, 191 (1938). The E_0 values are highest in perchloric acid, next in nitric acid and lower in sulfuric acid. The true equilibrium constant should take into account the effect of the anion. A simple formulation has been used here to illustrate the general nature of the calculations.

same number, a, moles of ferrous sulfate, then at equilibrium, if x is the moles of ceric ion left, x moles of ferrous ion will also remain, and the moles of cerous and ferric ions will each be equal to $(a - x)$. Then

$$K = \frac{[\mathrm{Ce}^{+++}]\,[\mathrm{Fe}^{+++}]}{[\mathrm{Ce}^{++++}]\,[\mathrm{Fe}^{++}]} = \frac{(a-x)}{x}\frac{(a-x)}{x} = \frac{[\mathrm{Ce}^{+++}]^2}{[\mathrm{Ce}^{++++}]^2} = \frac{[\mathrm{Fe}^{+++}]^2}{[\mathrm{Fe}^{++}]^2} = 10^{14.2};$$

and

$$\frac{a-x}{x} = 10^{7.1},$$

or, at equilibrium, the amount of ferric ion is approximately 10 million times that of the residual ferrous ion.

If a were 0.002M(= 0.1117 g. Fe per liter), x would be found from $0.002 - x = 10^{7.1}\ x$, or

$$(10^{7.1} + 1)\ x = 0.002$$

$$x = 1.6 \times 10^{-10} \text{ mole}$$

or about 0.000000009 g. per liter

In more complicated types of reaction the effect of hydrogen ion is considered separately as was done for the oxidation of arsenite, p. 212. The remainder of the process may be formulated: $a\mathrm{Ox}_1 + b\mathrm{Red}_2 \rightleftharpoons b\mathrm{Ox}_2 + a\mathrm{Red}_1$, with equilibrium constant, $K = \frac{[\mathrm{Red}_1]^a\ [\mathrm{Ox}_2]^b}{[\mathrm{Ox}_1]^a\ [\mathrm{Red}_2]^b}$. At the equivalence-point the ratio $\frac{[\mathrm{Red}_1]}{[\mathrm{Ox}_1]}$ is always equal to $\frac{[\mathrm{Ox}_2]}{[\mathrm{Red}_2]}$ because the reactants at this particular point have been brought together in the ratio of the coefficients a and b of the equation for the reaction. Since the substances react in the ratio $a : b$, the amounts that remain unchanged at equilibrium will also stand in ratio $a : b$. The equilibrium concentrations of the substances may then be represented below the equation:

$$\begin{array}{lcccc} & a\mathrm{Ox}_1 & + \quad b\mathrm{Red}_2 & \rightleftharpoons a\mathrm{Red}_1 & + \quad b\mathrm{Ox}_2 \\ \text{Equilib. conc's} & (a - ax) & (b - bx) & ax & bx \text{ moles} \end{array}$$

where a and b are, of course, small whole numbers. In the ratios

$\frac{[\mathrm{Red}_1]}{[\mathrm{Ox}_1]} = \frac{ax}{a - ax}$, and $\frac{[\mathrm{Ox}_2]}{[\mathrm{Red}_2]} = \frac{bx}{b - bx}$ the *a*'s and *b*'s cancel out and each ratio $= \frac{x}{1 - x}\cdot$ Hence *K* may be set equal to either

$$\left(\frac{[\mathrm{Red}_1]}{[\mathrm{Ox}_1]}\right)^{a+b} \quad \text{or} \quad \left(\frac{[\mathrm{Ox}_2]}{[\mathrm{Red}_2]}\right)^{a+b},$$

or alternatively:

$$\frac{[\mathrm{Red}_1]}{[\mathrm{Ox}_1]} = \frac{[\mathrm{Ox}_2]}{[\mathrm{Red}_2]} = \sqrt[a+b]{K}.$$

K is calculated from the apparent E_0 values of the two systems at the acidity in question. For any desired *K*, it is possible to calculate how great the spread must be between the two E_0 values.

REVIEW QUESTIONS AND PROBLEMS

1. Derive the changes in oxidation number for the following processes in acidified solutions:
   (a) Sodium bismuthate to form bismuth nitrate.
   (b) Potassium iodate to form iodine monochloride.
   (c) Antimonous acid to form antimonic acid.
   (d) Hydroxylamine (NH_2OH) oxidized to nitrate.
   (e) Sodium thiosulfate oxidized to sodium tetrathionate.

2. Write balanced equations, (a) molecular and (b) ionic, for the following reactions:
   (a) Potassium permanganate, vanadyl sulfate and sulfuric acid.
   (b) Potassium bichromate, potassium iodide in 0.5–1.5 *M* HCl.
   (c) Potassium iodate, arsenious acid in 4–6 *M* HCl.
   (d) Ceric sulfate and antimonous chloride in *M* sulfuric acid.
   (e) Potassium bromate and arsenious acid in HCl solution.

3. Calculate the grams per liter of 0.1 *N* solution for (i) Potassium iodate when reduced (a) to iodine monochloride, and (b) to iodine. (ii) Potassium permanganate when reduced to MnO_2. (iii) Ceric sulfate.

4. If a solution is 0.1 molar in ferric ion, 0.05 molar in stannous ion, and 1 *M* in acid at the moment of mixing, how much ferric ion will remain in (a) moles per liter and (b) gram per 100 ml. after equilibrium has been established?

   Ans. (a) Approx. 1×10^{-8} mole, (b) 5.5×10^{-8} g.

5. Calculate how much ferrous ion, (a) in gram and (b) in moles per liter, will remain when 25 ml. of 0.1 *M* ceric sulfate has been mixed with 25 ml. of 0.1 *M* ferrous sulfate. (Use the standard potentials in Table XIV, pp. 208-209.)

6. The equilibrium constant for the reaction between arsenious acid

and iodine is $K = \dfrac{[H_3AsO_4]\,[I^-]^3\,[H^+]^2}{[H_3AsO_3]\,[I_3^-]} = 0.16$. When equivalent amounts of iodine and arsenious acid have been mixed, as shown by the starch end-point, calculate approximately the ratio of arsenic acid to arsenious acid at hydrogen-ion concentrations of 10^{-8}, 10^{-6} and 10^{-3} *M*, respectively. (Note. At the starch end-point a slight excess of iodine or tri-iodide ion amounting to about 2×10^{-5} mole per liter is present, and the iodide concentration may be taken as 0.1 *M*.) Which $[H^+]$ is correct and how may it be maintained?

7. What substances are quantitatively oxidized by iodine in *N* acid solutions? In neutral solutions? What substances are reduced quantitatively in *N* acid solution by an equivalent quantity of potassium iodide?

8. List the various methods that may be used to detect the end-point in the reaction between ceric sulfate and ferrous sulfate in *N* acid solution. Which is probably the most convenient, and which the most accurate?

9. Criticize the following procedures: Stannic chloride is reduced with potassium iodide and the iodine is titrated with standard sodium thiosulfate. A sulfide is fused with sodium carbonate and the sulfate is precipitated with barium chloride.

10. Calculate the potential at which not more than 0.001 per cent of the iron in a 0.1 *M* ferrous sulfate solution will remain unoxidized. What is the theoretical E_0 value of a reagent that will oxidize ferrous iron to this extent at the equivalent point? (Note which of the common oxidizing agents have an E_0 value equal to or higher than that calculated.)

11. Stannous chloride is known by experiment to be a much better reducing agent than is stannous sulfate under similar conditions. Give a probable cause of this difference in behavior of the two salts.

12. If 50 ml. of a solution 0.1 *M* in Fe^{+++} is mixed with 50 ml. of a solution 0.1 *M* in Cu^+, calculate the equilibrium concentration of Fe^{+++} in moles per liter and in grams per 100 ml.

13. Calculate the extent to which 0.1 *M* ceric sulfate in 1 *N* sulfuric acid might be reduced by interaction with water or its ions in the sense of a process like: $4Ce^{++++} + 2H_2O \rightleftharpoons O_2 + 4Ce^{+++} + 4H^+$. How may this calculation be interpreted in view of the known properties of ceric solutions, Chap. XIII? Also see "overvoltage."

Ans. $\dfrac{[Ce^{+++}]}{[Ce^{++++}]} = 10^{3.57}$; i.e., practically complete reduction if equilibrium were established.

14. Calculate the equilibrium ratio of titanic to titanous chloride in a solution 0.1 *M* in both titanic and chromous chlorides and 1 *M* in HCl at the moment of mixing, at 25° C.

15. Would it be possible to use *o*-phenanthroline ferrous sulfate as indicator for the titration of ferrous ion in the presence of vanadyl ion without oxidizing the latter?

16. Suggest a method for determining the amounts of both iron and vanadium in a mixture without employing a physical chemical method of indication. See Fig. 49.

CHAPTER XI

OXIDATIONS WITH POTASSIUM PERMANGANATE

Standard Potassium Permanganate. Potassium permanganate is a valuable and powerful oxidizing agent. Its solutions are fairly stable and their intense color makes the use of an indicator unnecessary. As little as 0.01 ml. of a 0.1 *N* permanganate solution imparts a visible pink color to 100 ml. of water. Titrations with this reagent are generally carried out in an acid medium, with consequent reduction to a manganous salt. Sulfuric acid is the most suitable acid because it does not act on permanganate in dilute solution. Hydrochloric acid sometimes causes complications on account of its reducing action:

$$(1)\quad 2KMnO_4 + 16HCl = 2KCl + 2MnCl_2 + 5Cl_2 + 8H_2O,$$

some of the permanganate being used up in the formation of chlorine as well as in the titration. Occasionally potassium permanganate is used as an oxidizing agent in neutral solution, and is then reduced to manganese dioxide.

Potassium permanganate is seldom free from manganese dioxide, and in any case traces of dust and organic matter in the water cause more or less reduction to this oxide. Therefore a permanganate solution is never made up exactly by weight, but after removal of the manganese dioxide is standardized against arsenious oxide, sodium oxalate or pure electrolytic iron. Other substances have been proposed for this standardization, such as Mohr's salt, $(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$, and oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, the disadvantages of which are evident. Iron wire, which is sometimes used, cannot be recommended as it contains carbon and varies widely in composition. Owing to the difficulty of obtaining pure iron and to the comparative ease of obtaining pure sodium oxalate, $Na_2C_2O_4$, and arsenious oxide, As_2O_3, the latter have been adopted by the Bureau of Standards as the most suitable substances for the standardization of permanganate solutions.

$$(2)\quad 5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4$$
$$= 10CO_2 + 5Na_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

$$(3)\quad 5H_3AsO_3 + 2KMnO_4 + 6HCl = 5H_3AsO_4 + 2KCl$$
$$+ 2MnCl_2 + 3H_2O.$$

Sodium oxalate is anhydrous, can be heated to 240° C. without decomposition, and gives a colorless solution which is perfectly stable. The oxalate is converted into sodium carbonate by ignition, and is therefore of value also as a standard in acidimetry.

Arsenious oxide is readily obtained pure, can be dried at 105°-110° C. and is also an excellent primary standard for iodine solutions. Because it is not readily soluble in water it is dissolved in alkali to form a soluble arsenite, which is then acidified to form arsenious acid. The reaction between permanganate and arsenious acid does not proceed according to equation (3) unless a suitable catalyst is present. Otherwise the manganese is reduced to a valence between three and four. A very small amount of potassium iodide or iodate,[1] is a suitable catalyst.

A solution of potassium permanganate, once properly prepared, is quite stable as long as it is completely protected from dust and from strong light. For this purpose, a special arrangement is required which provides for the washing of all air entering the bottle and for the removal of the solution through a glass siphon or similar device. If these precautions are not taken, a solution of permanganate will gradually deposit manganese dioxide and become weaker; therefore it should be standardized about the time it is used. Permanganate must never come in contact with organic matter such as rubber, paper, etc. (Why?)

Uses of Potassium Permanganate. Potassium permanganate may be used in acid solution to oxidize Mn^{II} to Mn^{III}, Fe^{II} to Fe^{III}, Sb^{III} to Sb^{V}, As^{III} to As^{V}, Cu^{I} to Cu^{II}, Sn^{II} to Sn^{IV}, Ti^{III} to Ti^{IV}, Mo^{III} or Mo^{V} to Mo^{VI}, U^{IV} to U^{VI}, V^{II} or V^{IV} to V^{V}, $H_4Fe(CN)_6$ to $H_3Fe(CN)_6$, HCNS to HCN + H_2SO_4; H_2O_2 to

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[1] R. Lang, Z. anal. Chem. **152,** 197 (1926).

$H_2O + O_2$, $H_2C_2O_4$ to $CO_2 + H_2O$, HI to I_2; in neutral or alkaline solution to oxidize NO_2^- to NO_3^-, I^- to IO_3^-; and in neutral or slightly acid solution to oxidize Mn^{II} to MnO_2.

Preparation of 0.1 *N* Potassium Permanganate. When reduced to a manganous salt, the equivalent of potassium permanganate has already been shown (p. 193) to be $\frac{KMnO_4}{5}$ or 31.605; therefore a liter of 0.1 *N* solution should contain, theoretically, 3.1605 g. Weigh out about 3.3 g. of the crystals and dissolve in 200 ml. of warm, distilled water. Pour the solution into a 1000 ml. beaker or cylinder, and dilute to 1 liter. Mix the liquid thoroughly and let it stand for at least 24 hours, or preferably for two or three days, so that all organic matter in the water will be oxidized, and the manganese dioxide will completely settle. Filter the clear solution through an unweighed Gooch crucible prepared as described on p. 30, or a glass or porcelain filtering crucible. Avoid paper, which reduces permanganate. Instead of filtering the solution, the clear portion may be siphoned off through a siphon composed entirely of glass, into a clean, glass-stoppered bottle. If the latter process is used, the end of the tube must be at least 2 or 3 cm. above the bottom of the cylinder so that the precipitate of manganese dioxide is not disturbed. Keep the solution in the stoppered bottle in the locker; cover the neck of the bottle with a small beaker as a protection against dust.

In a buret read the upper level of the liquid instead of the bottom of the meniscus because of the deep color. Do not return unused solution from the buret to the storage bottle.

Standardization of the Permanganate Solution. *Procedure Using Arsenious Oxide.*[1] A special reagent grade of arsenious oxide is used for this purpose. Dry it in the oven at 105°-110° C. for one or two hours. Weigh from a weighing bottle three samples of about 0.25 g. each into a 400 ml. beaker or 500 ml. conical flask. Dissolve in 10 ml. of water 3 g. of crystallized sodium hydroxide or pellets free from oxidizing or reducing substances, and add the solution to the arsenious oxide. Let it stand for 8 to 10 minutes, stirring occasionally. Be sure that no particles of the oxide remain on the sides of the beaker. When

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[1] H. A. Bright, Bur. Standards J. Research, **19**, 691 (1937); Ind. Eng. Chem. Anal. Ed. **9**, 577 (1937).

solution is complete add 100 ml. of water, 10 ml. of hydrochloric acid (sp. gr. 1.18) and one drop of 0.0025 *M* potassium iodate, iodide, or iodine chloride. Titrate with the permanganate solution until a faint pink color persists for 30 seconds. Add the last ml. dropwise, allowing time for each drop to decolorize before making further addition. The small correction due to the excess of permanganate required to color the solution can be determined by running a blank, using the same amounts of water, reagents and catalyst. It should amount to less than 0.03 ml.

If osmium tetroxide is used as catalyst, only sulfuric acid must be present.

Calculation of the Normality. The equivalent of arsenious oxide is one-fourth of the molecular weight or 49.455 g.; 1 ml. of normal solution contains the milliequivalent, or 0.049455 g. If the weight of the sample is divided by the number of ml. of permanganate solution used, the weight of arsenious oxide equivalent to 1 ml. of permanganate is found. If this last value is then divided by the m.e. of arsenious oxide, the normality of the permanganate solution is obtained.

Procedure Using Sodium Oxalate.[1] A special grade of sodium oxalate of accurately known purity is used for this purpose. Dry the material in the oven at 105°-110° C. for 2 hours or more. (How high a temperature may be used without danger of decomposition?) Weigh from a weighing bottle three samples of about 0.3 g. each into 500 ml. conical flasks or 400 ml. beakers, add 250 ml. of dilute sulfuric acid (5 ml. per 100 ml.) previously boiled 10-15 minutes and then cooled to 27° C. ± 3°. Stir until the oxalate has dissolved. Add 39-40 ml. (or all but a few ml.) of 0.1 *N* permanganate at a rate of 25-35 ml. a minute, while stirring slowly. Let stand until the pink color disappears (about 45 seconds). If it does not disappear, discard this sample and begin another, adding a few ml. less of the permanganate solution. Heat to 55°-60° C. and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 1 ml. of oxidizing agent slowly with particular care to allow each drop to be completely decolorized before the next drop is added. Care should also be taken to prevent the forma-

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[1] R. M. Fowler and H. A. Bright, Bur. Standards J. Research, **15**, 493 (1935).

tion of a brown film of manganese dioxide, caused by the permanganate running down the side of the flask. Do not allow the solution in the beaker to cool below 55° C. by the time the end-point is reached.

Calculation of the Normality. It is evident from equation (2) that the equivalent of sodium oxalate is one-half of the molecular weight, $\frac{134.0}{2}$ or 67.00 g.; 1 ml. of normal solution contains the milliequivalent, or 0.06700 g. If the weight of the sodium oxalate sample is divided by the number of ml. of permanganate solution used, the weight of the oxalate equivalent to 1 ml. of permanganate is found. If this last value is then divided by the m.e. of sodium oxalate, the normality of the permanganate solution is obtained. The results should check within two parts in a thousand. The average of the results of the standardizations should be taken.

DETERMINATION OF IRON IN IRON OXIDE OR ORE. PERMANGANATE TITRATION METHOD

Principle. As has already been stated (p. 201 ff.), it is often necessary to reduce a metal to a certain definite state of oxidation before titrating it with permanganate. Iron is such a metal, and since ferrous salts are so readily oxidized, even by the oxygen of the air, special precautions are necessary to make sure that all of the iron is present in the ferrous form. The oxide is dissolved in hydrochloric acid because sulfuric acid is almost without action.

$$(4)\quad Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$

Since the absence of hydrochloric acid is very desirable, the chloride is converted to the sulfate by evaporation with an excess of sulfuric acid:

$$(5)\quad 2FeCl_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 6HCl.$$

A number of reducing agents for the ferric ion are available, such as zinc, cadmium, mercury, aluminum, lead, stannous chloride, hydrogen sulfide, or sulfurous acid, but those most commonly used are zinc, cadmium, aluminum, or stannous chloride.

(6) $Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4$.

(7) $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

After the reduction is complete, the excess of reducing agent must be removed. Any excess of metal is removed by dissolving all of it, or by removing that which remains undissolved; excess of hydrogen sulfide or of sulfurous acid, by boiling in a current of carbon dioxide to prevent oxidation by the air; and excess of stannous chloride, by oxidation with mercuric chloride to stannic chloride.

(8) $SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2$.

The mercurous chloride, being insoluble, has very little reducing action under the conditions of the titration.

Potassium permanganate is immediately added to the *cold,* ferrous sulfate solution until all ferrous iron is oxidized to the ferric form. The slightest excess of reagent will impart its characteristic color to the solution.

(9) $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 +$
$2MnSO_4 + K_2SO_4 + 8H_2O$.

If zinc is used, the reduction is usually carried out in a "Jones Reductor," a long tube containing a column of amalgamated zinc in granular form. Wire of cadmium, zinc, or aluminum, in the form of a spiral or a chain, is more convenient as it is very easily removed after the reduction is finished. Zinc and cadmium, free from iron, are obtainable, but a correction must always be applied for the small amount of iron in the aluminum dissolved.[1] Zinc usually contains a little lead which is liberated as the zinc dissolves and floats about in the solution, causing trouble. Amalgamation. of the zinc decreases this difficulty. Hydrochloric acid solutions dissolve zinc and aluminum so rapidly that much of the metal is wasted.[2] Cadmium wire dissolves slowly, but its action in reducing ferric solutions is somewhat slower.

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[1] Specially pure aluminum wire may be obtained from J. T. Baker Chemical Co.

[2] Very pure aluminum and zinc dissolve rather slowly.

Care must be taken to prevent oxidation of the ferrous sulfate, which would occur if the solution were allowed to stand for a time.

Since the evaporation of the chloride with sulfuric acid lengthens the process considerably, it is desirable, if possible, to avoid this step and to use the hydrochloric acid solution directly. As already stated, however, hydrochloric acid reduces permanganate, and causes the results for iron to be high. If the concentration of hydrochloric acid is small and the solution cold, this error may not be very large, and it may be reduced to a negligible quantity by the addition of manganous sulfate which lowers the oxidation potential of the permanganate and thereby makes it a weaker oxidizing agent. The tendency of the permanganate to oxidize chloride is decreased, but its action on ferrous iron is still rapid.[1] In this method, the ferric chloride is reduced by stannous chloride, and the excess of the latter removed by mercuric chloride, as previously described; then sulfuric acid, manganous sulfate, and phosphoric acid are added. The latter, by forming a complex ion with ferric ion bleaches out the yellow color in the solution, and thus causes the end-point to be more distinct. The main purpose of the phosphoric acid, however, is to lower the oxidation potential of the ferric-ferrous system, and make the ferrous ion a stronger reducing agent. Thus there is less opportunity for the permanganate to react with the chloride. This method gives excellent results if the following precautions are observed:

1. As much hydrochloric acid as possible must be removed by evaporation.
2. Only a very slight excess of stannous chloride must be added. Otherwise a heavy precipitate of mercurous chloride will form and will in part be reduced to mercury. Both the mercurous chloride and mercury will exert a noticeable reducing action on the ferric salt.
3. The solution must be cold and dilute.
4. Sufficient manganous sulfate and phosphoric acid must be added.
5. The permanganate must be added slowly and with constant stirring.

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[1] Barneby, J. Am. Chem. Soc. **36**, 1429 (1914).

Owing to the many precautions required and to the fleeting nature of the end-point, this method does not give as good results in the hands of a beginner as the method in which ferrous ion is titrated in sulfuric acid solution with permanganate. The student should be able to explain the necessity for each of these precautions.

Errors. (Those that may occur in the method involving reduction of ferric ion with aluminum, zinc, or cadmium in sulfuric acid solution.) If all of the hydrochloric acid is not removed, it will reduce some of the permanganate.

The reduction of ferric ion may be incomplete. There is no means of knowing just when the action is finished and it should be allowed to continue for a short time after all the yellow color disappears.

The solution may be oxidized, especially when hot, by too long exposure to the air. Cold solutions are more stable.

Too much sulfuric acid causes the end-point to be indistinct; 3 to 5 ml. of the acid gives the most satisfactory results.

The end-point is not permanent because of the following reaction, which is, however, very slow in cold acid solution:

$$(10)\quad 2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4.$$

Other Applications. This method may be applied with proper modifications to the titration of compounds of Sb^{III}, Mn^{II}, Cu^{I}, Mo^{V}, Mo^{III}, Ti^{III}, U^{IV}, V^{IV}, V^{II}; it may also be applied to the acids mentioned on pp. 221-222. The method may be used to titrate Sn^{II} and As^{III}, but better procedures are available.

The following oxidizing agents may be determined by the addition of a measured excess of standard ferrous sulfate, the excess of the reducing agent being titrated with standard permanganate: permanganates, manganese dioxide and other higher oxides, chromates, persulfates, and chlorates. In the case of chromic acid, direct titration is possible. Ferrous sulfate is more stable if it contains a considerable amount of sulfuric acid, but it must always be standardized the same day it is used.

Procedure. Weigh out three samples of 0.35 to 0.4 g. each into 150 ml. beakers. Add 10 ml. of water and 20 ml. of concentrated hydrochloric acid. Cover the beaker and keep the material just below the boiling point on a suitable hot-plate until dissolved. The time required for the solution of the sample, usually one-half to one hour, will depend upon the temperature, the reaction at room temperature being extremely slow. Do not allow the solution to evaporate to less than 5 to 10 ml.; add more acid if necessary. Rotate the liquid in the beaker vigorously to see if all iron oxide has dissolved. Any undissolved particles will collect in the center. The heating must be continued until no dark particles remain[1] (Equation (4)). Cool the solutions, add 4 ml. of concentrated sulfuric acid and evaporate to slight fumes of this acid on a low temperature hot-plate (Equation (5)). Care must be taken not to heat too strongly, for then the mass is liable to spatter, and it will be difficult also to dissolve the residue afterwards. Hang three glass hooks over the edge of the beaker to facilitate evaporation, and place a watch glass on these hooks. Glass hooks are made by bending small glass rods (never tubing) into a U, and by cutting off the arms unevenly so that one is about 15 mm. and the other about 20 mm. in length. The ends of the hooks should be rounded in the flame. The shorter arm is always placed inside the beaker. The beginner is likely to heat the moist residue at too high a temperature or for too long a time, or else to stop heating before all the hydrochloric acid is expelled. It is neither necessary nor desirable to evaporate off much sulfuric acid, and fumes of it will usually not be noticeable. The residue should be somewhat moist with sulfuric acid. As the hydrochloric acid escapes, the color of the mixture becomes lighter, until there remains a light-yellow or straw-colored mass of ferric sulfate and sulfuric acid. If no pungent odor of hydrochloric acid can be detected from the material when still warm (not hot), all chloride has been removed. If the material is very hot, the irritating fumes of sulfuric acid will be noticeable. All hydrochloric acid will be expelled before sulfuric acid begins to volatilize. (Why?) The watch-glass cover should be dry.

To the cool residue add cautiously 25 ml. of water, remove the glass hooks and heat the material until all the ferric sulfate is dissolved. Replace the water lost by evaporation. A trace of flocculent silica may be disregarded. The time required for

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[1] If there are insoluble dark particles that may have to be treated further, filter the diluted solution through paper, wash the residue and fuse it using the technique described on p. 246.

dissolving the sulfate may vary from 20 minutes to many hours and will depend upon the extent to which the solid salt was heated. If the ferric sulfate does not dissolve after being heated for a number of hours, add hydrochloric acid, which will dissolve it readily, and evaporate the liquid again. Take care this time not to apply too much heat. The solution of ferric sulfate may be reduced in two ways: with cadmium, aluminum, or amalgamated zinc wire, or by passing it through a Jones reductor.

Reduction with Cadmium, Zinc, or Aluminum Wire. Transfer the solution, not over 100 ml. in volume, to a 250 ml. conical flask and insert a spiral containing at least 1 meter of pure aluminum, cadmium or amalgamated zinc wire,[1] having a diameter of 2.5 to 3 mm. If smaller spirals are used, two or three may be required. The wire should be bent into a hook at one end so that the spirals may be easily lifted out of the flask. Cover the flask with an inverted crucible cover and boil the solution gently. Continue the application of heat for 10 or 15 minutes after the solution has become colorless (Equation (6)); do not let it evaporate to any extent. Cool the flask and liquid quickly under the tap, remove and rinse off the cover; then lift out the spiral with a glass rod provided with a hook on one end, while rinsing it carefully with cold water during its removal. Titrate the solution at once (why?) with 0.1 *N* potassium permanganate to the first change in color, a faint brownish or yellowish pink, which persists for 15 to 20 seconds (Equation (9)). The pink color is modified by the yellow color of ferric sulfate which is, however, much less pronounced in a cold than in a hot solution. The end-point is very sharp against a white background in good light. Do not overstep the end-point; if this happens, the analysis must be rejected. From the result obtained with the first sample, the volumes of permanganate required for the others may be estimated approximately and the end-points approached more rapidly. It is best to standardize the oxidizing solution within two or three days of the time it is to be used. The spiral should be cleaned by brushing. After rinsing, it is ready for further use. If ordinary aluminum wire is used, the dry spiral must be weighed to within 0.02 g. before and after use. The percentage of iron in it is determined

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[1] **Smith and Rich, J. Chem. Ed. 7, 2948 (1930).**

by a blank titration and the proper correction subtracted from the volume of permanganate used in titrating each sample.

Reduction by the Jones Reductor. This apparatus (see Fig. 51) consists of a tube, 18 to 20 mm. in diameter and 35 to 45 cm. long, provided at the bottom with a stop-cock; just above the stop-cock there is a perforated disk with an asbestos pad, on which rests a column of 20-30 mesh zinc, which has been amalgamated with 0.1 to 1 per cent of mercury by being shaken with the proper amount of 2 per cent mercuric chloride or mercuric nitrate.[1] This zinc column should be 30 to 40 cm. in length.

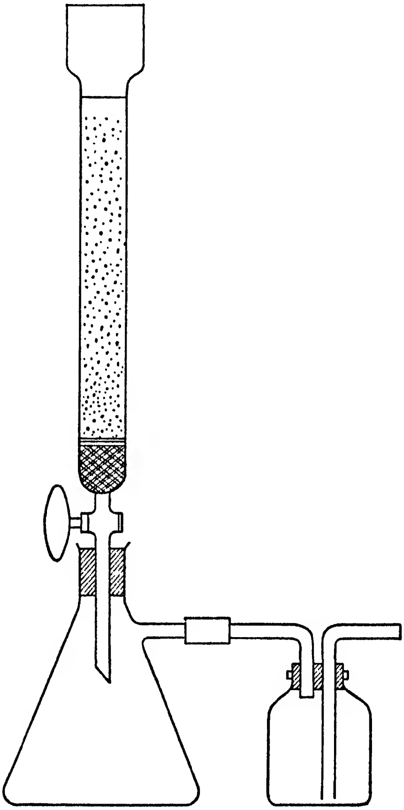

Fig. 51. Jones Reductor.

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[1] H. W. Stone and D. N. Hume, Ind. Eng. Chem. Anal. Ed. **11,** 598 (1939), have studied the effect of varying the proportion of mercury in zinc amalgam.

The tube below the stop-cock passes through a rubber stopper into a 500 ml. suction flask, which is connected with a filter pump the suction of which can be regulated by a pinchcock. After 50-100 ml. of a warm 2 or 3 per cent solution of sulfuric acid has been drawn through the tube, remove the receiver and add a drop of permanganate which should tint the solution. If the permanganate is decolorized, further washing is necessary. The apparatus is then ready for use.

Dilute the ferric sulfate solution to 100 ml.; pass a little dilute sulfuric acid—2 to 3 per cent—through the reductor and then draw through the ferric sulfate solution, which must be at room temperature, at the rate of 75 to 100 ml. a minute. Finally pass 25 to 50 ml. of 2 to 3 per cent sulfuric acid and 100 to 150 ml. of water through the tube. Remove the reductor from the flask, and titrate the solution of ferrous sulfate immediately with standard permanganate as directed in the first method. Wash the reductor again and test the washings with a drop of the permanganate solution to be sure that all of the sample was washed through. The zinc reductor must always be kept filled with water, and if it has not been used for some time, considerable acid may have to be drawn through it.

Calculation of Results. Since the reaction involves the oxidation of ferrous iron, the equivalent of iron is its atomic weight, or 55.85 g. (What would that of ferric oxide be?) The milliequivalent is therefore 0.05585 g. (What is the m.e. of ferric oxide?) The volume of the permanganate used is multiplied by its normality in order to find the volume of normal solution to which it is equivalent. If this latter volume is multiplied by the m.e. of iron, the weight of iron in the sample is obtained. From this the percentage is calculated as usual. The note-book must contain all the data for the standardization of the permanganate solution.

DETERMINATION OF HYDROGEN PEROXIDE

Hydrogen peroxide reacts with permanganate according to the following equation:

$$(11)\quad 5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

The determination of the concentration of commercial 3 per cent peroxide is a simple titration. Weigh a small stoppered flask, pipet into it about 2 ml. of peroxide solution and weigh it again. Rinse the sample into a 250 ml. beaker or flask to which has previously been added 2-3 ml. of concentrated sulfuric acid and 75 ml. of water. Titrate with 0.1 *N* permanganate to the first pink tinge. The m.e. of hydrogen peroxide is 0.01701 g. Calculate the percentage of it in the solution.

Small amounts of organic substances are often added to commercial hydrogen peroxide to render it more stable. Since these organic substances may react to some extent with permanganate, this titration may not give accurate results.

SUGGESTIONS REGARDING THE SOLUTION OF PROBLEMS INVOLVING A CHANGE IN EQUIVALENT

A problem of very useful type for practice in volumetric calculations is that which involves a change in equivalent. In the solution of such problems, the following principle should be remembered in addition to those principles already mentioned:

If a substance is determined by two different volumetric reactions and if the equivalent of the substance is different in each of these reactions, the number of ml. of solution of the same normality, equivalent to the same weight of the substance. will vary inversely as the numbers or fractions which express the equivalents in terms of gram molecular weights.

This will be evident if one considers that the lower the equivalent the more standard solution will be required to titrate a given weight of a substance.

The following problems will illustrate the application of this principle:

1. A certain weight of chromic acid, H_2CrO_4, required 40 ml. of 0.1 *N* alkali for neutralization. How many ml. of 0.1 *N* reducing agent would be required for the reduction of the same weight of chromic acid to chromic chloride?

$$\text{Equivalent of } H_2CrO_4 \text{ in acidimetry reaction} = \frac{H_2CrO_4}{2}$$

$$\text{Equivalent of } H_2CrO_4 \text{ in reduction reaction} = \frac{H_2CrO_4}{3}$$

$$40 : x :: 1/3 : 1/2.$$

$x = 60$ ml. of 0.1 *N* reducing agent required.

2. One gram of solution containing ferric chloride and free hydrochloric acid requires 50 ml. of 0.1 *N* alkali for complete neutralization of the free acid and the acid obtained by hydrolysis. The iron in another 1 g. sample requires 10 ml. of 0.1 *N* permanganate for titration. Calculate the percentages of ferric chloride and hydrochloric acid.

$$\text{Equivalent of } FeCl_3 \text{ against } KMnO_4 = \frac{FeCl_3}{1} = 162.2.$$

$$\frac{0.1622 \times 10 \times 0.1 \times 100}{1} = 16.22 \text{ per cent } FeCl_3.$$

$$\text{Equivalent of } FeCl_3 \text{ against alkali} = \frac{FeCl_3}{3}.$$

$$10 : x :: \tfrac{1}{3} : 1.$$

$x = 30$ ml. of 0.1 *N* alkali for $FeCl_3$.
$50 - 30 = 20$ ml. of 0.1 *N* alkali for free hydrochloric acid.

$$\frac{0.03647 \times 20 \times 0.1 \times 100}{1} = 7.29 \text{ per cent hydrochloric acid.}$$

3. Fifty ml. of dilute permanganate is added to sulfurous acid and the excess of the latter boiled off. The free sulfuric acid formed required 18 ml. of 0.1 *N* alkali for titration. Calculate the normality of the permanganate when used to titrate oxalic acid.

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O.$$

$$\text{Equivalent of } KMnO_4 \text{ against alkali (acidimetry)} = \frac{KMnO_4}{2}$$

$$\text{Equivalent of } KMnO_4 \text{ against } H_2C_2O_4 \text{ (reduction)} = \frac{KMnO_4}{5}$$

$$18 : x :: \tfrac{1}{5} : \tfrac{1}{2}.$$

$x = 45$ ml. of $KMnO_4$, 0.1 *N* against oxalate, or 4.5 ml. of *N* solution.

$$\frac{4.5}{50} = 0.09\,N$$

REVIEW QUESTIONS AND PROBLEMS

1. How many ml. of 0.0950 *N* permanganate standardized against arsenious oxide would be required for the titration of (*a*) 2.1500 g. of 2.80 per cent hydrogen peroxide, (*b*) 1.050 g. of $K_4Fe(CN)_6$?

2. One gram of a solution containing Na_3AsO_3 and Na_2CO_3 requires 50.00 ml. of 0.1000 *N* acid for titration using methyl orange as indicator. The Na_3AsO_3 in 1 g. requires, after being acidified, 20 ml. of 0.1000 *N* $KMnO_4$ for oxidation. Calculate the percentage of each salt present.

Ans. 10.60 per cent Na_2CO_3, 19.19 per cent Na_3AsO_3.

3. Ten grams of a solution containing hydriodic acid, HI, and sulfuric acid requires 95.00 ml. of 0.1000 *N* alkali for neutralization and 90.00 ml. of 0.1000 *N* permanganate for conversion of iodide to iodate. Calculate the percentage of each acid present.

4. A precipitate of calcium oxalate, CaC_2O_4, is contaminated with calcium carbonate and silica. 0.6400 g. requires 80.00 ml. of 0.1000 *N* permanganate for titration. The same weight after ignition to oxide requires 92.80 ml. of 0.1000 *N* acid for neutralization. Calculate the percentage of calcium oxalate and carbonate present in the precipitate.

5. Fifty ml. of permanganate which is 0.1000 *N* against oxalate is allowed to react with excess of manganous sulfate as follows:

$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4.$$

How many ml. of 0.1000 *N* alkali would be required to neutralize the acid formed in this reaction?

Ans. 20.00 ml.

6. If 30.00 ml. of 0.1000 *N* alkali is formed in the following reaction: $2KMnO_4 + KI + H_2O = 2KOH + 2MnO_2 + KIO_3$, what weight of potassium iodide is present?

7. Ten g. of a solution containing only HCNS, HCl and water requires 40.00 ml. of normal silver nitrate to precipitate both, and 60.00 ml. of normal oxidizing agent to convert the HCNS into HCN + H_2SO_4. What percentage of each acid is present?

8. Of an aqueous solution containing formic acid, HCO_2H, and sulfuric acid, 10.00 g. requires 30.00 ml. of 0.1000 *N* alkali for neutralization and 20.00 ml. of 0.1000 *N* oxidizing agent to convert the formic acid to carbon dioxide and water. Calculate the percentage of each acid present in the solution.

9. A solution of permanganate is 0.1500 *N* against ferrous sulfate What is its normality if used (*a*) to titrate manganous sulfate, thus $2KMnO_4 + 3MnSO_4 + 2ZnO = K_2SO_4 + 5MnO_2 + 2ZnSO_4$; (*b*) to titrate manganous fluoride, thus: $KMnO_4 + 4MnF_2 + 8HF + 9KF = 5K_2MnF_5 + 4H_2O$?

Ans. (*a*) 0.0900 *N*, (*b*) 0.1200 *N*.

10. Ten g. of a solution containing only hydroferrocyanic acid, sulfuric acid and water requires 15.00 ml. of 0.1000 *N* permanganate to oxidize the hydroferrocyanic acid. Another 10 g. sample requires 70.00 ml. of 0.1000 *N* alkali to neutralize completely both acids. What is the percentage of each acid present?

Ans. 3.240 per cent $H_4Fe(CN)_6$ and 0.490 per cent H_2SO_4.

11. Sixty ml. of potassium tetroxalate solution ($KH_3(C_2O_4)_2 \cdot 2H_2O$) 0.1000 *N* against alkali require 40.00 ml. of permanganate solution for titration of the oxalate. Calculate the normality of the permanganate.
Ans. 0.2000 *N*.

12. In the determination of iron by titration with permanganate what error will be caused by the unsuspected presence of 1 per cent of trivalent arsenic?
Ans. 1.49 per cent.

13. In the determination of calcium oxide by titration of the oxalate with permanganate what error will be caused by the unsuspected presence of 1 per cent potassium thiocyanate referred to the weight of the sample.

14. What must be the normality of a permanganate solution so that 1 ml. = 1 per cent of iron when a 0.5000 g. sample is taken?

15. Complete and balance equations numbered 6–15 on p. 286.

16. A 0.3500 sample containing only iron and ferric oxide was dissolved, reduced to the ferrous state and titrated with 0.1100 *N* permanganate, of which 50.00 ml. was required. Calculate the percentages of Fe and Fe_2O_3 in the sample.

17. One ml. of permanganate solution is equivalent to 0.004000 g. of arsenious oxide. To how much ferric oxide is it equivalent? What is its normality?

18. One g. of a mixture of metallic silver and silver oxide was dissolved in a large excess of ferric sulfate, and the ferrous sulfate formed by the action of the metal required 25.00 ml. of 0.0900 *N* permanganate. What per cent of metallic silver was present?

19. Show by a hypothetical equation the number of electrons gained or lost (*a*) when permanganate is reduced to trivalent manganese, (*b*) when stannous tin is oxidized to the stannic state. Define an electron. Write the corresponding hypothetical equations involving available oxygen.

20. If the oxidation-reduction potentials of two systems are so far apart that a quantitative reaction between them appears possible, and yet no such reaction actually occurs, how might this difficulty be overcome? Illustrate by an example.

DETERMINATION OF CALCIUM OXIDE IN CALCIUM CARBONATE

Principle. The reaction used in standardizing a permanganate solution is of value for titrating not only sodium oxalate, but also oxalic acid and all oxalates that are decomposed by sulfuric acid. The reaction serves therefore to determine calcium, copper, lead, zinc, and other metals. It happens, however, that calcium is the only common metal that is best precipitated in this way, so that in this case the method is of particular importance.

The calcium is precipitated as the oxalate by neutralizing with ammonia the acid solution containing an excess of oxalic acid. (See p. 339 ff.) The precipitate is washed with cold water and is dissolved in hot, dilute, sulfuric acid:

(12) $CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4$.

The oxalic acid liberated is titrated with standard potassium permanganate:

(13) $5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$.

Errors. The errors due to adsorption of silica or to the incomplete dissociation of the carbonate, which are so important in the gravimetric method, p. 339 ff, are avoided here. Any coprecipitation of other oxalates, such as that of magnesium, will obviously introduce similar errors in both methods. Filter paper, if present, may cause a slight reduction of the permanganate if the titration is unduly prolonged.

Interfering Substances. With the exception of the alkalis, all the common metals form insoluble oxalates. Magnesium oxalate is appreciably soluble, but if much of it is present two precipitations are required to obtain pure calcium oxalate. All other metals should therefore be absent.

Procedure. Weigh out three samples of 0.35 to 0.4 g. into 400 ml. beakers. Add 20 ml. of water, cover the beaker with a watch glass, add 5 ml. of concentrated hydrochloric acid, and heat until the sample has dissolved. Rinse down the sides of the beaker and the cover, and dilute to 250 ml. Heat the solution to boiling and add about 1 g. of ammonium oxalate or 0.9 g. of oxalic acid dissolved in 25 ml. of water. Filter this solution if it is not perfectly clear. This quantity of oxalate represents a considerable excess, and part of the calcium is usually precipitated in this acid solution. Add slowly to the hot solution, from a buret, a filtered solution of dilute ammonia—5 ml. of concentrated ammonia to 50 ml. of water—at the rate of about 5 ml. per minute, until the liquid is neutral or faintly alkaline. A few drops of methyl red should be added as an indicator. Let the solution stand for an hour in a warm place to be assured of complete precipitation of the oxalate. Test with a few drops of ammonium oxalate solution for complete precipitation. If it should be necessary to leave the solution over night, do not keep it warm.

Another method of neutralizing the solution, which is less troublesome than the slow addition of ammonia, consists in adding 10 to 15 g. of urea, $(NH_2)_2CO$, after the addition of ammonium oxalate. The solution is kept at the boiling point to cause hydrolysis of the urea into carbon dioxide and ammonia. When the color of the indicator shows that the solution is neutral, the heat is removed.

Decant the clear, supernatant liquid through a filter; discard the filtrate after testing it for calcium. Transfer the precipitate to the filter by a jet of water from the wash bottle, rub loose with a rubber-tipped rod all particles adhering to the beaker, transfer these to the filter, and wash the precipitate on the paper ten times with cold water to remove ammonium oxalate. (Test?) Direct the wash water around the edge of the filter paper each time. Unfold the damp filter on the side of a 400 ml. beaker, and wash the precipitate into the beaker with a jet of water. Prepare in a separate beaker a solution of 60 ml. of water and 5 ml. of concentrated sulfuric acid. Heat this to about 70° C., and let this acid solution drip from a stirring rod onto the filter to dissolve all traces of the precipitate (Equation (12)). Wash the filter once more with water and then reject it. The acid solution may be clear, or, if sufficiently concentrated, it may contain a white precipitate of calcium sulfate in suspension. Dilute the solution to 200 ml., heat nearly to boiling and titrate the oxalic acid with 0.1 N permanganate solution (Equation (13)). Observe the precautions given for the titration of sodium oxalate on p. 223. From the result of the first titration, estimate approximately the volumes of permanganate required for the others. After dissolving the calcium oxalate in acid, do not allow the solution to stand over night before titration.

Calculation of Results. Since one mole of calcium oxalate yields one of oxalic acid, both substances have an equivalent of one-half the molecular weight, as is evident from the equation: $H_2C_2O_4 + O = H_2O + 2CO_2$, in which $1H_2C_2O_4$ requires 2 equivalents of oxygen. Since one mole of calcium oxalate yields one of calcium oxide, the latter must have an equivalent of $\frac{56.08}{2}$ or 28.04 g. The m.e. of calcium oxide is therefore 0.02804. The volume of permanganate used is converted into its equivalent of normal solution and the calculation carried out as in the determination of iron.

DETERMINATION OF AVAILABLE OXYGEN IN MANGANESE DIOXIDE OR PYROLUSITE

Principle. The pure mineral, pyrolusite, is composed of manganese dioxide. All of the oxygen above the amount required to form manganous oxide, MnO, with the manganese present is called available oxygen, because only this excess is available for oxidation purposes. For many purposes the value of the oxide used depends upon its percentage of available oxygen, which is usually expressed as percentage of manganese dioxide. It was stated on p. 227 that higher oxides such as manganese dioxide could be determined by reduction with an excess of standard ferrous sulfate. This excess of reducing agent is determined by titration with standard permanganate solution. The disadvantage of using ferrous sulfate is that the operation must be carried out in an atmosphere free from air in order to prevent the oxidation of ferrous sulfate by oxygen from this source. An atmosphere of carbon dioxide is commonly used. A reducing agent which is stable in air and is also a primary standard is more convenient. Sodium oxalate is such a substance. The sample of manganese dioxide is heated in a dilute sulfuric acid solution with a known weight of sodium oxalate until all the dioxide has dissolved:

(14) $MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$.

The excess of oxalate is titrated with 0.1 N permanganate by the method used in standardizing the latter.

Errors. If the solution is heated too long or at too high a temperature, or if the sulfuric acid is too concentrated, some of the oxalic acid may be decomposed. Moreover, if the sample is not finely powdered, it may not be completely reduced except after too prolonged digestion.

Interfering Substances. Other higher oxides or strong oxidizing agents will also oxidize the oxalic acid.

Other Applications. This method can be used to determine available oxygen in other higher oxides such as PbO_2 and Pb_3O_4.

Procedure. From the very finely powdered material which has been dried at 110°-120° C., weigh samples of about 0.5 g. each into 250 ml. conical flasks. Add to each sample approximately 1 g. of dried sodium oxalate (primary standard), accurately weighed. Pour into the flask 100 ml. of 4 *N* sulfuric acid and heat the material on a steam bath or low temperature hot plate, with occasional shaking, until all black or dark brown particles have dissolved. Disregard a white, or light brown residue. The time for complete solution will vary from 15 minutes to 2 hours and will depend upon the fineness of the sample, the temperature, and the amount of agitation of the solution. Titrate the hot solution with 0.1 *N* potassium permanganate, as was done in standardizing the latter.

Calculation of Results. The m.e. of sodium oxalate is 0.06700 g. If the weight of sodium oxalate added is divided by this number, the quotient will be the volume of normal permanganate solution required, if no manganese dioxide were present. The difference between this volume and that of permanganate solution actually used, after converting the latter into its equivalent of normal solution, is the volume of normal solution required to reduce the manganese dioxide in the sample. The equivalent of manganese dioxide is one-half its molecular weight; the m.e. is 0.04346 g. The percentage of manganese dioxide in the sample should be reported.

REVIEW QUESTIONS AND PROBLEMS

1. A 1.0500 g. sample of magnetite, Fe_3O_4, is dissolved in hydrochloric acid in the absence of air and, without further treatment, titrated with 0.1080 *N* permanganate, of which a volume of 7.01 ml. is required. What is the percentage of magnetite present, assuming that it has the above formula?

2. A sample of MnO_2 is reduced by heating in hydrogen to MnO, with a loss of 0.0960 g. What volume of normal ferrous sulfate would have been required to titrate the available oxygen?

Note.—Do not take into account the molecular weight of these oxides.

3. The arsenic in 1.5000 g. of ore is precipitated as arsenious sulfide, which is oxidized to arsenate and sulfate by adding 115.00 ml. of *N* permanganate. Thirty ml. of normal ferrous sulfate is required to titrate the excess of permanganate. What is the per cent of arsenic in the ore?
Ans. 30.32 per cent.

4. One g. of a mixture containing only calcium oxalate and lead oxalate requires 88.00 ml. of 0.1250 *N* permanganate. What is the per cent of each oxalate present?

Ans. 47.86 per cent of CaC_2O_4 and 52.14 per cent of PbC_2O_4.

5. The precipitate of calcium oxalate from 1.0565 g. of limestone requires 40.25 ml. of 0.2080 *N* permanganate. What per cent of calcium oxide in the limestone?

6. A sample of pure calcium carbonate loses 0.3500 g. when ignited to oxide. How much 0.2500 *N* permanganate would be required to titrate it if it were precipitated as oxalate? How much 0.2500 *N* acid would be required to neutralize the oxide?

7. What will be the error in the determination of calcium oxide in a 1.0000 g. sample if the precipitate, assumed to be pure calcium oxalate when titrated with permanganate, actually contains magnesium oxalate equivalent to 20.0 mg. of magnesium oxide?

Ans. 2.78 per cent too high.

8. A sample of hydrogen peroxide required for titration 82.50 ml. of 0.1065 *N* permanganate. What weight of oxygen would it have evolved if it had been heated until completely decomposed? What volume would the gas have occupied under standard conditions?

CHAPTER XII

OXIDATIONS WITH POTASSIUM BICHROMATE

Chromic acid, H_2CrO_4, and its salts, although not as strong oxidizing agents as permanganate, have certain advantages over the latter. Potassium bichromate, $K_2Cr_2O_7$, can easily be obtained pure, is stable up to its fusion point, and is, therefore, an excellent standard in oxidimetry.[1] Willard and Young have shown that the C.P. and "reagent quality" potassium bichromate on the market are sufficiently pure for use directly as a primary standard.[2] Solutions can be made by weight and these undergo little or no change on standing. The bichromate is used only in acid solution and is reduced to a chromic salt; it is not reduced by cold, moderately dilute hydrochloric acid, and consequently titrations can be carried out in a hydrochloric acid solution as satisfactorily as in the presence of any other acid.

$$(1)\quad 6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O.$$

When ferrous iron is to be titrated in a hydrochloric acid solution, stannous chloride is generally used to reduce the ferric ion. Minute quantities of ferrous salts in such a solution can be detected by the formation of a blue precipitate of ferrous ferricyanide, upon addition of potassium ferricyanide:

$$(2)\quad 2K_3Fe(CN)_6 + 3FeCl_2 = Fe_3(Fe(CN)_6)_2 + 6KCl.$$

This is a method of detecting ferrous iron, not bichromate. The ferricyanide cannot be added to the solution to be titrated, for the blue precipitate of ferrous ferricyanide is not acted on by excess of bichromate. It is necessary to use the ferricyanide as an external indicator, by removing and testing a drop of the solu-

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[1] McCroskey, J. Am. Chem. Soc. **40**, 1662 (1918); Vosburgh, *ibid.*, **44**, 2120 (1924).

[2] Willard and Young, Ind. Eng. Chem. Anal. Ed. **7**, 57 (1935).

tion from time to time. At first a blue precipitate will form but this becomes fainter and fainter, and it finally disappears when the end-point is reached. Obviously it is much more troublesome to use an external indicator; moreover such a procedure removes some of the solution, which cannot be returned. This method is, therefore, seldom used in titrating iron.

Diphenylamine or diphenylbenzidine, when used as internal indicator, gives with ferrous and ferric salts a greenish color, which is changed to a deep blue by a slight excess of oxidizing agent.[1] An indicator with such properties is more convenient than ferricyanide. The blue color is due to the formation of an organic oxidation product, and the color reaction of the indicator is reversible so that back titration with ferrous sulfate is possible if the end-point is overstepped. See p. 199.

Diphenylamine sulfonic acid[2] has several advantages over the two indicators just mentioned. It is soluble in water, more rapid in reaction, and not susceptible to the inhibiting effect of mercuric chloride, tungsten, or moderate changes in *p*H. With all these indicators, the presence of considerable phosphoric acid or of a fluoride is necessary in order to reduce the concentration of ferric ion by forming a complex. Otherwise the ferric ion, because of its tendency to oxidize the indicator, prevents a sharp end-point reaction.

Preparation of 0.1 *N* Potassium Bichromate. This salt contains 6 equivalents per molecule, as shown by the equation: $Cr_2O_7^{=} + 14H^{+} + 6e = 2Cr^{+++} + 7H_2O$. The equivalent of potassium bichromate is therefore one-sixth of the molecular weight, $\frac{294.21}{6}$ or 49.035 g., and one liter of 0.1 *N* solution will contain 4.9035 g. Weigh into a weighing bottle 3 or 4 mg. more than the theoretical amount of pure potassium bichromate and dry in the oven at 110° C. for not less than two hours. Weigh the bottle and salt, empty the salt into a small beaker and weigh the bottle again. Dissolve the salt in warm water, transfer the solution carefully to a liter volumetric flask, and dilute to the mark at room temperature. Mix the solution thoroughly and pour it into a dry liter bottle; label with date of preparation and normality. Cal-

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[1] Knop, J. Am. Chem. Soc. **46**, 263 (1924); Mehlig, J. Chem. Ed. **3**, 324 (1926). See also page 199.

[2] Sarver and Kolthoff, J. Am. Chem. Soc. **53**, 2902, 2906 (1931).

culate the normality by dividing the actual weight of the potassium bichromate used by the theoretical weight for one liter of normal solution, 49.035 g.

DETERMINATION OF IRON IN IRON ORE. BICHROMATE TITRATION METHOD

Principle. Iron ores may be divided into three classes:

1. Anhydrous oxides such as hematite, Fe_2O_3, or magnetite, Fe_3O_4.
2. Hydrated oxides, such as limonite, $2Fe_2O_3 \cdot 3H_2O$.
3. Carbonates of iron (ferrous), such as siderite, $FeCO_3$.

Ores in the first group must be finely powdered to facilitate solution, as they dissolve in acid with much greater difficulty than do those in the second or third group. Hydrochloric acid is the best solvent; nitro-hydrochloric is much less efficient, and nitric or sulfuric acid is almost without action. A high temperature greatly hastens the process of solution, but the temperature is limited by the low boiling point of hydrochloric acid. If potassium bisulfate, $KHSO_4$, which has been heated to form potassium pyrosulfate, $K_2S_2O_7$, is used, a much higher temperature, even a red heat, may be attained without driving off too much of the acid. On account of the difficulty of fusing large samples of ores, the pyrosulfate is used only to dissolve the iron in the siliceous residue, obtained after treatment of the main portion of the ore with hydrochloric acid. By fusion of the ore with an alkali an oxide is obtained which dissolves more readily in acid than the original material. All iron ores, if finely powdered, may be dissolved in hydrochloric acid without any preliminary treatment. Those given out are ready for use after drying. The addition of stannous chloride hastens solution, but care must be taken not to use too much.

After the ore is dissolved, the ferric chloride is reduced with a very slight excess of stannous chloride,

$$(3)\quad 2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4;$$

this excess is then oxidized with mercuric chloride.

$$(4)\quad 2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

The ferrous chloride solution is titrated with 0.1 *N* bichromate, and diphenylamine sulfonic acid is used as oxidation-reduction indicator. The insoluble siliceous residue may contain iron. If white, the residue is disregarded, although even then it may contain silicates of iron which can be decomposed only by the use of hydrofluoric and sulfuric acids. If not white, it is fused with potassium pyrosulfate, which dissolves any iron present in a form other than silicate; the fused material is dissolved in hydrochloric acid and added to the main solution of the ore.

Errors. Reduction may be incomplete if too little stannous chloride has been added. This condition will always be made evident by the fact that no precipitate of mercurous chloride forms when mercuric chloride is added. The error cannot be corrected by the addition of more stannous chloride, since it will react with the mercuric chloride and not with the ferric chloride.

A heavy precipitate of mercurous chloride or even of free mercury may appear if too much stannous chloride has been added. Both of these substances, because of their reducing action, cause the results to be too high.

$$(5)\quad HgCl_2 + SnCl_2 = Hg + SnCl_4.$$

A large excess of acid is detrimental, since the stronger oxidizing action produced by the acid causes the indicator to be destroyed in part and increases the blank.

The reduced solution may be partly oxidized by too long exposure to the air, before or during titration, and too low results be obtained. Too much of the solution may be removed for tests when an external indicator is used.

If ferricyanide solution is used, it must be fresh and not more concentrated than 0.1 per cent. Otherwise the end-point will be indistinct. Excessive amounts of oxidation-reduction indicators should be avoided. The error due to uncertainty in the end-point may be practically eliminated by standardizing the bichromate solution by the same procedure against electrolytic iron.

If any platinum is present in the solution, as may be the case when a fusion has been made in a platinum crucible, a yellow color will result which cannot be removed by stannous chloride. Thus it will be impossible to ascertain sharply when sufficient stannous chloride has been added.

Other Applications. This process may be reversed and used for the determination of chromium—a more common use than for the titration of iron. All volumetric methods for chromium are alike in one respect—the chromic salt obtained by dissolving the alloy or ore is oxidized to chromic acid, H_2CrO_4, the excess of the oxidizing agent is removed, and the chromic acid is titrated with a reducing agent such as standard ferrous sulfate. In the case of steels and other alloys containing chromium, a reagent is needed which will oxidize the chromium in a sulfuric or nitric acid solution. If chloride ion is present, the chromium is not oxidized. Steels are dissolved in dilute sulfuric acid, the ferrous salt and carbonaceous matter oxidized with nitric acid, and then one of the following oxidizing agents is added to oxidize the chromic salt:

Persulfate with a little silver nitrate, excess removed by boiling:

(6) $Cr_2(SO_4)_3 + 3(NH_4)_2S_2O_8 + 8H_2O + (AgNO_3) =$
$2H_2CrO_4 + 3(NH_4)_2SO_4 + 6H_2SO_4.$

In this reaction a manganous salt, if present, is oxidized to permanganate. This latter substance which would also react with the standard ferrous sulfate, is reduced before titration by boiling the solution for a few minutes after the addition of a few drops of hydrochloric acid, the silver chloride present acting as catalyst, or by the use of sodium azide. Chloride ion in small quantity has no effect on chromic acid in dilute solution.

Permanganate, excess reduced, on boiling the solution, to manganese dioxide, which is filtered off:

(7) $5Cr_2(SO_4)_3 + 6KMnO_4 + 16H_2O = 10H_2CrO_4 +$
$6MnSO_4 + 3K_2SO_4 + 6H_2SO_4.$

(This is not a volumetric reaction.)

The action of permanganate with manganous sulfate in boiling-hot solution is

(8) $2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 +$
$2H_2SO_4.$

Concentrated, boiling *perchloric acid* which is also used to oxidize chromium in steel has no oxidizing action on manganese.

Chrome iron ore, $Cr_2O_3 \cdot FeO$, is best decomposed by fusion with sodium peroxide, which converts the chromium into chromate. Excess of peroxide is destroyed by boiling the solution. Sodium peroxide has little effect on steel and it is not a satisfactory oxidizing agent for a solution of steel, because so much hydrous ferric oxide is precipitated.

After the chromium in any of these materials has been oxidized and the excess of oxidizing agent has been removed, the chromic acid is titrated with ferrous sulfate which has been standardized against potassium bichromate. If preferred, a measured excess of standard ferrous sulfate may be added and the excess titrated with standard bichromate or permanganate. Diphenylamine, diphenylbenzidine, or diphenylamine sulfonate are used as indicators in either procedure, but trio-ortho-phenanthroline ferrous complex can be used only in a solution very strongly acid with sulfuric acid to increase the oxidation potential of chromic acid.

Procedure. Weigh out three samples of 0.35 to 0.4 g. each into 400 ml. beakers, add 25 ml. of concentrated hydrochloric acid and 5 ml. of water. Cover the material and keep it just below boiling until entirely dissolved. The time required for solution may vary from 30 minutes to several hours, and will depend on the character of the ore. Add more hydrochloric acid, if necessary, to replace that lost by evaporation. If the action seems to be very slow, even when the solution is hot, add a little stannous chloride occasionally; if, when the ore is dissolved, all yellow ferric chloride has disappeared, add a crystal of potassium chlorate. It is very important that the solution be kept as hot as possible without being actually boiled. When the ore is dissolved, a flocculent residue of siliceous material will remain, but no dark, heavy particles of the oxide. Since this residue usually contains a little iron, it should, in precise work, be decomposed by hydrofluoric and sulfuric acids in a platinum crucible. Any iron not present as a silicate may be removed by fusion with potassium pyrosulfate.

If the residue is not white, dilute the solution of the ore with an equal volume of water and filter into a 400 ml. beaker. Wash the residue with 1 per cent hydrochloric acid to remove the iron, then with water to remove the acid, and ignite the damp filter in a porcelain crucible to burn off carbon. If the residue is white, it may be rejected, as the previous color was due to organic matter. If it is colored, add to it about a gram of fused potassium bisulfate, or, more properly, pyrosulfate, $K_2S_2O_7$, and heat the mixture carefully until the salt fuses quietly and spattering ceases. Slowly raise the temperature of the covered crucible to a low red heat and keep the mass fused for 15 or 20 minutes. Sulfur trioxide is given off, and after a time the mass will begin to solidify, due to the presence of normal sulfate; the temperature must then be raised a little. Cool, dissolve in hydrochloric acid diluted with an equal volume of water, and add the solution to the main filtrate. The silica may be filtered out or may be allowed to remain. Concentrate the solution to 10 or 12 ml. All of the samples may be worked together to this point, but for the remainder of the experiment only one sample must be handled at a time. The others may stand as long as desired. Heat one solution nearly to boiling and add 0.5 *N* stannous chloride, one drop at a time, rotating the liquid constantly, until all ferric chloride is reduced and one drop of the reducing agent causes the color to change from yellowish to colorless or a very pale green. Then add one or two drops excess, but no more. This reduction is the most critical part of the process and special care must be taken to avoid a greater excess of stannous chloride. (Why?) The end-point, which must be exact to within one drop, can be made sharp by having the solution very hot and small in volume (about 10 to 12 ml.), as the color of the ferric chloride is most pronounced under these conditions. The reduction is very rapid in a hot solution, although not quite instantaneous. If the stannous chloride has little effect and more than 10-15 ml. is required, it has probably become oxidized to stannic chloride and a fresh supply should be obtained. Reduce only one sample at a time; set the others aside until this titration is finished. (Why?) It is an excellent plan to have all the reagents measured out in advance and everything in readiness, so that after the addition of stannous chloride no unnecessary delay occurs until the titration is finished. After the reduction add immediately 10 ml. of concentrated hydrochloric acid, rinse down the sides of the beaker and the cover, and dilute the solution with cold water to 250 ml. Add 5 ml. of a saturated solution of mercuric chloride to oxidize the excess of stannous chloride. A slight white precipitate of mercurous chloride is formed, the amount depending on how much excess of stannous chloride was added. A few seconds may be required for the precipitate to appear, but the reaction is complete in a minute or two. If a heavy precipitate forms, too much stannous chloride was added and the results will be inaccurate.

1. *Sodium Diphenylamine Sulfonate as Internal Indicator.* After oxidizing the excess of stannous chloride, as described, add to the solution 10 ml. of phosphoric acid, sp. gr. 1.37 (directions for preparation given below), and three-tenths of 1 ml. of 0.01 *M* diphenylamine sodium sulfonate. Add 0.1 *N* bichromate solution slowly, while stirring constantly, until the pure green color changes to a gray or greenish gray. It may even turn to a bluish green when much iron is present. Then add the bichromate very slowly, one drop at a time, until the first tinge of purple or violet-blue color appears and remains on stirring. This is the true end-point. Subtract 0.05 ml. from the volume of bichromate used as a blank for the indicator.

The phosphoric acid, sp. gr. 1.37, is prepared by mixing one volume of syrupy phosphoric acid, sp. gr. 1.70, with an equal volume of water.

The 0.01 *M* diphenylamine sodium sulfonate solution used as the indicator is prepared by dissolving 0.32 g. of the barium salt in 100 ml. of water. Five-tenths of a gram of sodium sulfate is added and the clear solution decanted from the barium sulfate.

Diphenylamine or diphenylbenzidine may be dissolved in concentrated sulfuric acid and the solution thus obtained diluted with glacial acetic acid. Either solution is used in much the same way as the diphenylamine sulfonate. The two former indicators have a number of disadvantages, as already mentioned, and the sulfonate is to be preferred.

2. *Ferricyanide as External Indicator.* Although this indicator is not recommended because it is much less convenient than an internal indicator, and has, therefore, been largely superseded by the latter, the procedure is given as a convenient example of the technique involved in the use of an external indicator.

Have ready a solution of potassium ferricyanide made by dissolving in 50 ml. of water 0.03 to 0.04 g. of the crystals, which have been rinsed previously with distilled water to remove ferrocyanide. This solution will keep only a few hours and must not be more concentrated than these prescribed proportions. Half fill 10 or 15 of the depressions in a spot plate with it, or place drops of it on any white surface that has been paraffined to prevent the solution from spreading. The drops should be 6 or 7 mm. in diameter. As soon as the reaction between the stannous chloride and mercuric chloride is complete, titrate the solution with 0.1 *N* bichromate while stirring constantly (Equation (1)). At intervals take out with a stirring rod a drop of the solution and allow it to fall on a drop of the ferricyanide without stirring. A dark-blue precipitate will appear (Equation (2)). Continue adding the bichromate, 2 ml. at a time, until a drop removed from the solution shows a light-blue test with ferricyanide; then make a test after the addition of every two drops of bichromate to the solution, and when near the end-point, after every drop. When no blue or greenish-color appears in the test, the end-point has been reached. Be careful not to transfer any of the ferricyanide to the solution. Even when no ferrous ion is present, a blue or greenish color will often appear after long standing of a test portion, due to decomposition of the ferricyanide.

One of the most common sources of error is failure to stir the solution long enough to ensure thorough mixing with each drop of bichromate. More stirring is necessary than one would expect—at least several seconds of vigorous action.

To form a drop of suitable size for a test, take the rod out of the solution quickly in a nearly horizontal position; then hold it vertically over the drop of indicator.

The first titration will probably be somewhat inaccurate on account of the time required (which allows some of the ferrous ion to be oxidized), the amount of solution removed for tests, and the uncertainty of the color change at the end-point. The results serve, however, as a basis for estimating approximately the amount of bichromate required for the other samples. These need not be tested until within 2 ml. or less of the end-point; then no appreciable error is introduced by removing the drops necessary for the tests.

Standardization of Bichromate Solution. If potassium bichromate of definite purity is obtainable, a standard solution prepared from a known weight of this primary standard needs no further check. Sometimes, however, suitable potassium bichromate is not available. For this reason, and also because a standardization against iron largely eliminates possible errors due to end-point and to certain other factors, it may be preferable in some cases to use the following method if pure iron is available. Electrolytic iron of a purity of 99.97 per cent or more can be prepared. Iron wire is sometimes suggested for this purpose but it is usually quite impure and varies so much in composition that it is useless as a primary standard.[1] Ammonium ferrous sulfate is also unreliable.

Weigh into 400 ml. beakers three samples of pure iron of approximately 0.25 g. each. Add 10 ml. of concentrated hydrochloric acid and 1 or 2 ml. of water. Cover the beaker with a watch glass and keep the material warm until the sample is dissolved. The time required for solution may be 15 minutes or longer and will depend upon the size of the pieces. Do not boil the solution. The iron dissolves to form ferrous chloride:

$$(9)\quad Fe + 2HCl = FeCl_2 + H_2.$$

Some of the chloride is oxidized by the air to ferric chloride:

$$(10)\quad 4FeCl_2 + O_2 + 4HCl = 4FeCl_3 + 2H_2O,$$

which must be reduced by stannous chloride. Follow the directions given under "Procedure for Iron in Iron Ore," pp. 246-247.

Review Questions and Problems

1. Why is it necessary to add phosphoric acid when titrating ferrous ion with bichromate and using diphenylamine sulfonate as indicator? How does this addition alter the shape of the titration curve? Why is this addition unnecessary when ortho-phenanthroline ferrous complex is used as indicator?

2. The lead in a sample weighing 1.0600 g. is precipitated as lead chromate, which requires 50.15 ml. of 0.1100 *N* ferrous sulfate for titration. Calculate the per cent of lead in the sample.

3. A sample of chromite ($FeO \cdot Cr_2O_3$) weighing 0.5300 g. was fused with sodium peroxide and the chromate titrated with 39.10 ml. of 0.2550 *N* ferrous sulfate. Calculate the per cent of chromic oxide, Cr_2O_3, in the sample.

4. In the determination of iron by bichromate 0.50 per cent of trivalent antimony was also oxidized. How much of an error was thus introduced?

5. In 1.0000 g. of a solution containing only chromic chloride, hydrochloric acid and water, the chromium after oxidation to chromic acid requires for titration 30.00 ml. of 0.1000 *N* ferrous sulfate. To another

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[1] Analyzed iron wire, 99.9 per cent pure, can be obtained from Mallinckrodt Chemical Works.

sample of the same size are added 75.00 ml. of 0.1000 *N* sodium hydroxide and excess of hydrogen peroxide thus:

$$2CrCl_3 + 10NaOH + 3H_2O_2 = 2Na_2CrO_4 + 6NaCl + 8H_2O.$$

The excess of alkali requires 15.00 ml. of 0.1000 *N* acid. Calculate the percentage of hydrochloric acid in the solution.

Ans. 3.65 per cent.

6. Calculate the concentration of potassium bichromate, 1 ml. of which is equivalent to 2.0 mg. of iron.

7. A solution contains only chromic acid, sulfuric acid and water. Ten g. requires 40.00 ml. of 0.1050 *N* ferrous sulfate for reduction of the chromic acid and another sample of the same size requires 35.00 ml. of 0.2000 *N* alkali to neutralize both acids. Calculate the percentage of each acid present.

Ans. 1.65 per cent H_2CrO_4; 2.058 per cent H_2SO_4.

8. Write equations for each step in the determination of chromium in steel. (A little manganese is always present.)

CHAPTER XIII

OXIDATIONS WITH CERIC SALTS

It has been known for a long time that ceric salts are very strong oxidizing agents, but their value in analytical procedures has been demonstrated only recently.[1] If an oxidizing agent is to be used extensively in analytical work, it must meet a number of requirements, among the more important of which are the following: (1) it must compare favorably in its properties with oxidizing agents already in use; (2) it must be available in some convenient form so that solutions of it can be prepared readily; (3) it must be either a primary standard or a substance which can be standardized easily, and preferably against a primary standard; (4) it must serve as its own indicator when the equivalence point is reached, or suitable indicators for use with it must be available; (5) it must react stoichiometrically with a considerable number of reducing agents. These points will be discussed.

Comparison of Ceric Salts with Potassium Permanganate. Previously the most useful of the strong, volumetric oxidizing agents has been potassium permanganate. Some of the advantages and disadvantages of ceric salts as compared with this reagent follow:

1. Ceric salts are very strong oxidizing agents in acid solution. Some of them are even stronger than potassium permanganate under similar conditions. Both of these substances in acid solution are much stronger oxidizing agents than potassium bichromate.

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[1] Among the important papers which have appeared on this subject are the following: Willard and Young, J. Am. Chem. Soc. **50,** 1322, 1334, 1372 (1928); *ibid.* **51,** 149 (1929); *ibid.* **55,** 3260 (1933); Furman and Wallace, *ibid.* **51,** 1449 (1929); Furman, *ibid.* **50,** 755 (1928); *ibid.* **52,** 2347 (1930); Kunz, *ibid.* **53,** 98 (1931); Gleu, Z. anal. Chem. **95,** 305 (1933); Smith and Getz, Ind. Eng. Chem. Anal. Ed. **10,** 191, 304 (1938).

2. Ceric salts, like potassium permanganate, with one possible exception, are not primary standards.

3. Acid solutions of ceric sulfate are stable over a period of years. Such solutions need not be protected from light and it has been shown that they may be boiled for a short time with no change in normality. Therefore an acid solution of ceric sulfate far surpasses a permanganate solution in stability. This is not true of the nitrate and perchlorate, however.

4. Ceric sulfate may be used to titrate reducing agents in the presence of a high concentration of hydrochloric acid. Permanganate solutions are useless under such conditions because the permanganate oxidizes the hydrochloric acid to chlorine.

5. There is but one possible valence change in the case of a ceric salt which is acting as an oxidizing agent, $Ce^{++++} + e = Ce^{+++}$, while with permanganate a number of reduction products are possible, and it is not always easy to regulate conditions so that only one reduction product is formed.

6. A ceric salt can serve as its own indicator only when the solution being titrated is colorless. An indicator is usually unnecessary with a permanganate solution.

7. Ceric salts can be used as volumetric reagents only in an acid medium, because in alkaline solution perceric compounds may be formed. Potassium permanganate, in contrast, is used in a neutral or alkaline solution, but much less frequently than in an acid solution.

8. Both oxidizing agents may be standardized against the primary standards, sodium oxalate, arsenious oxide and pure iron.

The work of Smith and Getz[1] shows that the anion present in ceric solutions has considerable effect on the oxidation-reduction potential. In normal acid solution the values are 1.44 volts for the sulfate, 1.61 volts for the nitrate and 1.70 volts for the perchlorate. The stability of the solutions decreases in this order.[2] Increase in the perchloric acid concentration from 1 *N* to 8 *N* increases the potential of this system to 1.87 volts; in nitric acid solution, however, it is decreased from 1.61 to 1.56 volts; in sulfuric acid there is a decrease of only 0.02

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[1] G. F. Smith and C. A. Getz, Eng. Chem. Anal. Ed. **10**, 191, 304 (1938).

[2] G. F. Smith and C. A. Getz, Ind. Eng. Chem. Anal. Ed. **12**, (1940).

volt. To explain these effects, Smith and Getz assume that ceric nitrate, for example, does not exist in solution as such but as hexanitrato ceric acid, $H_2Ce(NO_3)_6$, which dissociates to give mainly the nitrato cerate ion, $Ce(NO_3)_6^{--}$. The ammonium salts, $(NH_4)_2Ce(NO_3)_6$[1] and $(NH_4)_2Ce(SO_4)_3 \cdot 2H_2O$, are readily prepared and are commercially available; the perchlorate, however, is too unstable to be prepared in crystalline form.

The higher potentials of the nitrate and perchlorate salts are advantageous in titrations which are rather slow with the sulfate, as, for example, in the titration of oxalate and of vanadyl ions, because the titration can be performed at room temperature. In such cases it is advantageous to use the high potential indicator, nitro-o-phenanthroline ferrous salt (see pp. 199, 201).

Preparation of 0.1 *N* Ceric Sulfate. Formerly it was necessary to prepare ceric sulfate solutions from ceric oxide.[2] At the present time, ceric ammonium sulfate and other ceric salts can be purchased and a solution prepared by dissolving the salt in cold water containing sufficient of the corresponding acid to prevent any hydrolysis. These salts need not be of a high grade of purity. The presence of other rare earths causes no difficulty since these metals do not show variations in valence. Such a solution is more quickly prepared than a permanganate solution, because the latter, to remain stable, must be freed from manganese dioxide before being standardized.

Since the reaction involved in the use of ceric salts is $Ce^{++++} + e = Ce^{+++}$, the change in oxidation number is 1, and the equivalent weight of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ or $Ce(SO_4)_2$ is its molecular weight, 632.5 or 332.1. One liter of 0.1 *N* solution should contain, therefore, approximately 63 g. of the ceric ammonium sulfate or 33 g. of the anhydrous ceric sulfate.

Procedure. Add 28 ml. of concentrated sulfuric acid slowly to 500 ml. of water in a 1500 ml. beaker. Weigh out on the side-table balance 64-66 g. of ceric ammonium sulfate or 35-40 g. of ceric sulfate. Add the salt to the acid solution and stir until the solid has dissolved. Dilute with 500 ml. of water, mix the

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[1] G. F. Smith, V. R. Sullivan and G. Frank, Ind. Eng. Chem. Anal. Ed. 8, 449 (1936).

[2] Willard and Young, J. Am. Chem. Soc. 51, 149 (1929).

solution thoroughly and transfer it to a clean, glass-stoppered bottle. It can be standardized at once.

Standardization of Ceric Sulfate Solution. A solution of ceric sulfate may be standardized against any one of three primary standards: arsenious oxide, sodium oxalate, or electrolytic iron. Since the first two of these can be procured more easily, procedures involving their use will be given. Oxidation-reduction indicators are available for determining the end-point in any of these titrations.

(1) *Against Arsenious Oxide.* The arsenious oxide is dissolved in sodium hydroxide, and the solution acidified with sulfuric acid. Osmium tetroxide is added to catalyze the reaction, followed by *o*-phenanthroline ferrous sulfate as oxidation-reduction indicator, and the titration made at room temperature with ceric sulfate.[1]

(1) $As_2O_3 + 2NaOH = 2NaAsO_2 + H_2O.$
(2) $2NaAsO_2 + H_2SO_4 = 2HAsO_2 + Na_2SO_4.$
(3) $HAsO_2 + 2Ce(SO_4)_2 + 2H_2O = H_3AsO_4 +$
$Ce_2(SO_4)_3 + H_2SO_4.$

Procedure for Standardization against Arsenious Oxide. Weigh 0.20-0.30 g. samples of dried arsenious oxide, analytical reagent, into 400 ml. beakers. Add 20-30 ml. of water and 2 g. of sodium hydroxide crystals. Warm the mixture gently and stir until the arsenious oxide has dissolved. Be certain that no particles of arsenious oxide remain on the sides of the beaker. Dilute by adding 100 ml. of water. Then add 20-30 ml. of 5 *N* sulfuric acid, 2 drops of 0.01 *M* osmium tetroxide solution as catalyst, 2 drops of 0.025 *M* triortho-phenanthroline ferrous sulfate, and titrate with the ceric sulfate to be standardized. Before the titration is begun, the solution is pale pink in color, after the addition of a few drops of ceric sulfate the pink shade becomes much more pronounced, and at the end-point the change in color from pink to a very pale blue is extremely sharp.

The 0.01 *M* osmium tetroxide solution is made by dissolving 1 g. of osmium tetroxide (sometimes called perosmic acid) in 400 ml. of 0.1 *N* sulfuric acid.

The 0.025 *M* tri-ortho-phenanthroline ferrous sulfate (fer-

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[1] Gleu, Z. anal. Chem. **95**, 305 (1933).

roin) ($(C_{12}H_8N_2 \cdot H_2O)_3FeSO_4$) solution is prepared by dissolving the correct amount of ortho-phenanthroline ($C_{12}H_8N_2 \cdot H_2O$) in a 0.025 *M* aqueous solution of ferrous sulfate.[1]

(2) *Against Sodium Oxalate.* The reaction, which is similar to that used in standardizing a permanganate solution, may be represented by the following equation:

$$(4)\quad H_2C_2O_4 + 2Ce(SO_4)_2 = 2CO_2 + Ce_2(SO_4)_3 + H_2SO_4.$$

The oxalate, in a hot hydrochloric or sulfuric acid solution, is titrated with the oxidizing agent until one drop of it causes a change in color of the solution from colorless to a light yellow.[2]

If the solution is sufficiently hot, the slightest tint of yellow is easily seen. A blank determination for the end-point should be made and the volume of the reagent required, usually approximately 0.05 ml. of a 0.1 *N* solution, should be subtracted from the volume used in a standardization.

This same reaction between sodium oxalate and ceric sulfate may be carried out at a much lower temperature (50° C.) in a hydrochloric acid solution containing iodine monochloride as catalyst. Under these conditions the reaction is sufficiently rapid so that tri-ortho-phenanthroline ferrous sulfate may serve as indicator.[3] A temperature of about 50° C. is the most satisfactory, for at higher temperatures too much of the indicator is destroyed, while at much lower temperatures the reaction is not sufficiently rapid. High concentrations of sulfuric acid cause a slow reaction.

As has already been pointed out, no catalyst is needed in titrating oxalate with nitrato or perchlorato cerate at room temperature.

Procedure for Standardization against Sodium Oxalate. Weigh into 250 ml. beakers samples of sodium oxalate, analytical reagent, which will require 25-35 ml. of ceric sulfate for titration. If the ceric sulfate solution is 0.25 *M* in sulfuric acid, 40-50 ml. may be used in a titration. Add 10-20 ml. of concentrated hydrochloric acid, and 5 ml. of 0.005 *M* iodine chloride, and dilute to 100 ml. After heating the solution to 50° C. (use a thermometer

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[1] This indicator solution and various ceric salts may be obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio.

[2] Willard and Young, J. Am. Chem. Soc. **50**, 1322 (1928).

[3] Willard and Young, J. Am. Chem. Soc. **55**, 3260 (1933).

as stirring rod), add 1 drop of 0.025 *M* tri-ortho-phenanthroline ferrous sulfate and titrate with ceric sulfate until the solution is pale blue in color and there is no return of any pink color after an interval of one minute. If the temperature falls below 45° C., reheat the solution to 50° C.

The iodine chloride solution is prepared by dissolving 0.279 g. of potassium iodide and 0.178 g. of potassium iodate in 250 ml. of water and adding at once 250 ml. of concentrated hydrochloric acid.[1] The solution thus obtained is 0.005 *M* in iodine chloride. It is adjusted either potentiometrically by adding dilute potassium iodide or iodate, or according to a method described by Swift and Gregory.[2]

Other Methods for Standardizing Ceric Sulfate Solutions. A solution may also be standardized against arsenious oxide in a hydrochloric acid solution containing iodine chloride as catalyst with ortho-phenanthroline ferrous sulfate,[3] against potassium ferrocyanide [4] or against electrolytic iron which has been dissolved in hydrochloric acid, reduced with stannous chloride, etc., according to the procedure given under the "Determination of Iron in Iron Ore. Ceric Sulfate Titration Method," pp. 258-259.

Indicators for Use in Titrations Involving Ceric Salts. Diphenylamine, diphenylbenzidine, diphenylamine sulfonic acid, erio green, erioglaucine [5] and ortho-phenanthroline ferrous sulfate are suitable for the titration of ferrous ion, although the first two are affected by the presence of mercuric salts. Ortho-phenanthroline ferrous sulfate, with its high oxidation potential, is especially valuable in titrations involving ceric salts or permanganate, but with bichromate the reaction at the end-point is too slow. Ferric ion or other moderate oxidizing agents are without effect on this indicator, so that it is of much more general application than any of the others. The nitro derivative is useful only in nitric or perchloric acid solutions. These indicators have been discussed more fully on pp. 198 and 199.

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[1] G. S. Jamieson, "Volumetric Iodate Methods," The Chemical Catalog Co., New York, 1926, pp. 8, 9.

[2] Swift and Gregory, J. Am. Chem. Soc. **52**, 901 (1930).

[3] Willard and Young, J. Am. Chem. Soc. **55**, 3260 (1933).

[4] K. Someya, Z. anorg. allgem. Chem. **181**, 183 (1929).

[5] Furman and Wallace, J. Am. Chem. Soc. **52**, 2347 (1930).

DETERMINATION OF IRON IN IRON ORE. CERIC SULFATE TITRATION METHOD

Principle. The principle of the method and the errors involved have already been discussed under the bichromate titration method for iron, p. 243. The ferric solution may be reduced by a metallic reducing agent or by stannous chloride, since chloride does not interfere when the solution is titrated with ceric sulfate.

After the ore is dissolved the ferric chloride is reduced with a very slight excess of stannous chloride,

$$(5)\quad 2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4;$$

this excess is then oxidized with mercuric chloride:

$$(6)\quad 2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4.$$

The ferrous chloride is then titrated with 0.1 N ceric sulfate:

$$(7)\quad 2FeCl_2 + 2Ce(SO_4)_2 + 2HCl = 2FeCl_3 + Ce_2(SO_4)_3 + H_2SO_4$$

using one of the indicators previously mentioned.

Procedure. The procedure is identical in every respect with that for "Determination of Iron in Iron Ore. Bichromate Titration Method," pp. 246-249, except that ceric sulfate is substituted for the bichromate solution, and eriogreen, erioglaucine or ortho-phenanthroline ferrous sulfate may be used as indicator, if desired, instead of diphenylamine sulfonic acid. The red color of the ortho-phenanthroline complex changes at the end-point to a faint yellowish or, sometimes, greenish color, with a tinge of pink if more than a faint turbidity of mercurous chloride is present, due to a slight adsorption of the dye by the precipitate. On standing for a few minutes the red color returns, due to the reducing action of the mercurous chloride on the oxidized indicator. The addition of 10 ml. of concentrated hydrochloric acid before adding the indicator is desirable.

If eriogreen or erioglaucine is used the change from pale greenish yellow to orange or pale rose is not instantaneous but gives warning of the approach of the end-point: the danger of over-stepping the end-point is slight if the reagent is added drop by drop near the end of the titration.

Other Applications of Ceric Sulfate. A few of the reactions which have been studied are listed below. In each case ortho-phenanthroline ferrous sulfate indicator is used. These and others are mentioned in recent articles by Young and by Furman[1] and descriptions of new uses for this reagent are appearing continually in the literature.

Calcium may be precipitated as the oxalate, the precipitate filtered, washed, and dissolved in dilute hydrochloric acid, and the oxalic acid titrated with standard ceric sulfate.

(8) $CaC_2O_4 + 2HCl = H_2C_2O_4 + CaCl_2.$
(9) $H_2C_2O_4 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + 2CO_2 + H_2SO_4.$

Arsenic has already been mentioned under methods of standardizing ceric sulfate solutions.

Ferrocyanide may be titrated in a hydrochloric or sulfuric acid solution with standard ceric sulfate.

(10) $2K_4Fe(CN)_6 + 2Ce(SO_4)_2 + (H_2SO_4) = 2K_3Fe(CN)_6 + Ce_2(SO_4)_3 + K_2SO_4.$

Hydrogen peroxide may be titrated with standard ceric sulfate or the reverse titration made.

(11) $H_2O_2 + 2Ce(SO_4)_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2.$

Cerium is determined by oxidizing it to the ceric state with persulfate and a little silver nitrate as catalyst, removing the excess of persulfate by boiling and titrating the ceric sulfate with standard ferrous sulfate, using ortho-phenanthroline ferrous sulfate as indicator. The oxidation can also be effected by sodium bismuthate, the excess of which is removed by filtration.

REVIEW QUESTIONS AND PROBLEMS

1. Discuss the advantages and disadvantages of ceric sulfate as a volumetric oxidizing agent.

2. Why is the indicator nitro-ortho-phenanthroline ferrous sulfate not suitable for use with ceric sulfate, but satisfactory in solutions containing only nitrate?

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[1] Young, J. Chem. Ed. **11**, 466 (1934); Furman, Chapter II, Newer Methods of Volumetric Analysis (a translation of Neuere Massanalytische Methoden by Oesper), D. Van Nostrand Co., 1938.

3. In the determination of chromium 1.00 per cent of ceric cerium is also present and titrated simultaneously. What is the error introduced?

4. What is the normality of a ceric sulfate solution the number of ml. of which gives the percentage of iron in a sample weighing 0.6000 g.?

5. One g. of impure sodium azide, NaN_3, requires 90.00 ml. of 0.1600 *N* ceric sulfate for oxidation to nitrogen. What is the percentage purity?

Ans. 93.63 per cent.

6. Twenty-five g. of 80.00 per cent ceric oxide, CeO_2, is converted into ceric sulfate and diluted to one liter. What is the normality of the solution?

CHAPTER XIV

OXIDATION AND REDUCTION PROCESSES INVOLVING IODINE (IODOMETRY)

The determination of the iodine involved in certain reactions affords a basis for many valuable processes of volumetric analysis. These are called iodometric processes. They may be divided into two classes:

1. *Direct methods* in which a standard solution of iodine is used as an oxidizing agent, either in an acid or in a neutral solution. An example is the titration of sulfurous acid:

(1) $H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$

In all reactions of this type the iodine is reduced to an iodide. Among the reducing agents thus determined are sulfide, sulfite, thiosulfate, arsenite, ferrocyanide, stannous, and antimonous ions.

The reactions of iodine with the weakest reducing agents do not proceed to completion, since iodine is a comparatively weak oxidizing agent. With somewhat stronger reducing agents, complete reaction may occur only when the solution is kept neutral, as described on pp. 276-277. Examples are the iodometric titration of ferrocyanide, trivalent arsenic and antimony. On the other hand, reactions with strong reducing agents go to completion without difficulty, even in an acid solution. Examples of the latter are the iodometric titration of sulfurous acid, stannous chloride, and hydrogen sulfide.

2. *Indirect methods* in which oxidizing agents are allowed to react with a neutral or acid solution (usually the latter) of a soluble iodide. In such cases, an equivalent amount of iodine is liberated, and is then titrated with a standard reducing agent, usually sodium thiosulfate, which is oxidized to sodium tetrathionate:

(2) $K_2Cr_2O_7 + 6KI + 14HCl = 2CrCl_3 + 3I_2 + 8KCl + 7H_2O.$

(3) $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$

Since hydriodic acid is a strong reducing agent, it is possible by this general procedure to determine a very large number of oxidizing agents, among which are the following: iodine, chlorine, bromine, iodate, periodate, hypobromite, bromate, hypochlorite, chlorite, chlorate, persulfate, hydrogen peroxide, nitrite, arsenate, ferricyanide, chromate, permanganate, manganese dioxide and other higher oxides, ferric, cupric, and antimonic ions.

The potential of the normal iodine-iodide system, 0.535 volt, does not vary appreciably with a moderate change in *p*H, but the potential of oxidizing anions increases with increasing concentration of hydrogen ion. This point is illustrated in the discussion of the arsenate-arsenite system on p. 212. Arsenic acid can be completely reduced by an iodide only in a very strongly acid solution, at least 4 *N* hydrochloric acid. At a lower acidity the oxidation potential of the arsenic acid is too low for quantitative reduction. Many weak oxidizing anions can be completely reduced by an iodide if their oxidation potentials are raised to a maximum by the presence in the solution of a large amount of acid.

Washburn[1] has calculated that to attain an accuracy of 1 part per thousand in the titration of an arsenite with iodine, the *p*H of the solution must be between 4 and 9. Weak reducing agents such as an arsenite and antimonite can be completely oxidized by iodine only in a neutral solution in which the concentration of the hydrogen ion is so low that the oxidation potential of the reducing agent is a minimum, or its reducing power is a maximum. Strong reducing agents such as sulfurous acid can be completely oxidized by iodine even in strongly acid solution.

The potential of simple cations is not theoretically influenced by the concentration of hydrogen ion, but depends only upon the relative concentrations of the reduced and oxidized form of the cation, as, for example, $\frac{[\mathrm{Fe}^{+++}]}{[\mathrm{Fe}^{++}]}$. To reduce ferric ion completely, a high concentration of iodide ion is required; to prevent any reduction of ferric ion, a fluoride or phosphate is added, which will form with the ferric ion a complex or undissociated salt and will thus reduce its concentration to a very small value.

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[1] Washburn, J. Am. Chem. Soc. **30**, 31 (1908).

When it is difficult to obtain complete reduction of certain weak oxidizing agents, the completeness of reaction may be increased in one or more of the following ways:

1. The concentration of the hydrogen ion may be increased as just explained if this increases the oxidation potential of the oxidizing agent.
2. The concentration of the iodide ion may be increased, as, for example, in the reaction between ferric ion and iodide ion.
3. The iodine may be removed by boiling and then collected in an appropriate reagent, or it may be extracted with an immiscible solvent such as chloroform or carbon bisulfide.

In certain cases where an iodide is too strong a reducing agent, it becomes necessary to boil the oxidizing agent being analyzed with hydrochloric or hydrobromic acid and to pass the chlorine or bromine evolved into potassium iodide. The iodine thus liberated is titrated with thiosulfate solution. For example, manganese dioxide usually contains some ferric oxide; both oxides liberate iodine from hydriodic acid, but only the manganese dioxide liberates chlorine from hydrochloric acid.

The great advantage of iodometric processes lies in the sharp end-point that can be obtained. A drop of 0.1 *N* iodine solution imparts a perceptible color to 200 ml. of water and the test may be made still more sensitive by the addition of a solution of starch which forms, with iodine, a dark-blue adsorption complex containing both iodine and iodide, in which the iodine is so loosely adsorbed that it behaves like the free element. The solutions used in iodometry are fairly stable, and when certain precautions are observed some of these processes are among the most accurate in volumetric analysis.

It should be observed that all iodometric reactions are performed in either neutral or acid solution. If the solution is alkaline the iodine reacts with the hydroxyl ion present to form an iodide and hypoiodite:

$$(4)\quad I_2 + 2KOH = KI + KIO + H_2O.$$

The hypoiodite is extremely unstable and decomposes at once to form an iodate:

$$(5)\quad 3KIO = 2KI + KIO_3.$$

This decomposition occurs even in the presence of a normal carbonate owing to the hydrolysis of the latter, but is not significant in a solution containing a bicarbonate where the *p*H is not over 9.

As just stated, approximately neutral solutions are sometimes required in direct titrations with standard iodine and such solutions are ordinarily obtained by the use of various buffer mixtures. In the discussion on p. 129 ff it was demonstrated that the range of a buffer is determined by the ionization constant of the weaker constituent. The buffer mixtures most commonly employed to maintain a *p*H of approximately 7 are: 1. A solution of sodium bicarbonate saturated with carbon dioxide. 2. Borax and boric acid. 3. The two phosphates Na_2HPO_4 and NaH_2PO_4, in the proper proportions. When iodine is used in a direct iodometric titration, an iodide or hydriodic acid is formed. The latter substance will react immediately with the first buffer mixture to give carbonic acid, a volatile and very weak acid, and with the second mixture to give boric acid, also very slightly ionized. Thus in neither case would the *p*H of the solution be altered appreciably during the titration.

A very important source of error that occurs only in indirect iodometric reactions is the possibility of the liberation of iodine by the action of the oxygen of the air on hydriodic acid which is always present in considerable excess:

$$(6)\quad 4HI + O_2 = 2I_2 + 2H_2O.$$

This reaction does not occur in a neutral solution of pure potassium iodide, but it increases in velocity as the acidity of the solution increases, and it is hastened by strong light, and by the presence of certain impurities which act as catalysts, as, for example, traces of copper. Therefore the solution containing the excess of hydriodic acid must not be allowed to stand any longer than necessary before titration of the iodine with thiosulfate; if an appreciable period is required for the reaction between oxidizing agent and iodide to reach completion, an atmosphere of carbon dioxide should be provided. The importance of this "oxygen error" is evident from the fact that acid solutions are usually employed in indirect iodometric processes. In each of these cases cited acid solutions are used, although free chlorine and bromine will react with potassium iodide in a neutral solution.

The standard solutions generally used in iodometry are those of iodine and sodium thiosulfate; sometimes of sodium arsenite. Sodium thiosulfate is a better reducing agent than the latter, however, because it can be used to titrate an acid solution of iodine, whereas for sodium arsenite a neutral solution of iodine is required.

Starch Solution. A solution which is clear or only faintly opalescent is most satisfactory, and is readily prepared from soluble starch. Mix 5 g. of the solid very thoroughly with water and pour the paste, with constant stirring, into 500 ml. of boiling water. Allow the solution to cool, and add 10 g. of potassium iodide. Such a solution will keep a long time if stored under a layer of toluene in a stoppered bottle.

If ordinary starch is used, rub 2 g. into a thin paste with cold water, pour the paste slowly into 200 ml. of boiling water, and boil the liquid for two minutes. Let the solution settle and decant the clear portion. A fresh solution should be prepared each day, unless it is preserved by the addition of a few mg. of mercuric iodide.

According to Alsberg and Griffing[1] a starch solution may be prepared by stirring or shaking "puffed rice" with cold water for an hour, and filtering the mixture through a layer of "filter-cel." The clear solution thus obtained is preserved under toluene.

Certain precautions in the use of starch as an indicator should be mentioned. The solution should be fresh or should have been properly preserved. It must not be added to the solution being titrated until just before the end-point is reached. Otherwise some iodine may remain adsorbed even at the end-point. Starch cannot be used in a strongly acid solution because it hydrolyzes to form other products, nor can it be used in an alcoholic solution. There should be present in the starch solution at least 1 g. of potassium iodide per 100 ml. to obtain a proper color with iodine, since the blue adsorption compound contains iodide as well as iodine. When the first trace of iodine is added to a suitable starch solution, a pink color is obtained which becomes blue with the addition of more iodine. The color

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[1] Alsberg and Griffing, J. Am. Chem. Soc. **53**, 1401 (1931).

disappears on heating the solution. The same amount of starch should always be added in a titration. Two ml. of 1 per cent solution per 100 ml. of titrated solution is a satisfactory amount.

Standard Sodium Thiosulfate. When sodium thiosulfate reacts with rather weak oxidizing agents, it forms sodium tetrathionate, $Na_2S_4O_6$:

(7) $2Na_2S_2O_3 + O + H_2O = Na_2S_4O_6 + 2NaOH$
(also Equation (3)).

Since $2Na_2S_2O_3$ require 2 equivalents of oxygen, the equivalent of sodium thiosulate is its molecular weight. The crystallized salt has the formula $Na_2S_2O_3 \cdot 5H_2O$; its molecular weight is 248.19. One liter of 0.1 N solution will therefore contain 24.819 g. The solution cannot be made up exactly by weight, as the salt is efflorescent and its composition is, therefore, uncertain.

The reaction of sodium thiosulfate with weak oxidizing agents, such as iodine and ferric chloride, is as just given, but with stronger agents, such as bromine or bichromate, the reaction is no longer definite, as a considerable amount of sulfate is formed, together with other products. Thiosulfate can be completely oxidized to sulfate, but the reaction is not suitable for a volumetric process. The reagent is used therefore *only for titrating iodine in a more or less acid solution.*

Free thiosulfuric acid is very unstable:

(8) $H_2S_2O_3 = H_2SO_3 + S$.

A solution of a thiosulfate, when acidified, remains clear for a brief time; then free sulfur separates. In spite of this decomposition, thiosulfate may be used for titrating iodine in an acid solution if the solutions are so thoroughly mixed that there is no excess of thiosulfate present at any time. Thiosulfate solutions are stable as long as they are kept sterile. The bacteria which bring about decomposition seem to be less active between a pH of 9 and 10. Therefore the addition of a small amount of an alkali is beneficial. Oxygen has no effect on the solution.

Dissolve 24.85 g. of the pure crystals (weighed on side-table balance) in hot water which has been recently sterilized by boiling. Add to the solution 1 ml. of 0.1 N sodium hydroxide, or 0.1 g. of sodium carbonate, cool, and dilute to one liter. Allow the solution to stand in a stoppered bottle for a day or two before standardizing. It should be standardized within a day or two of the time it is used, to avoid possibility of change in the normality due to bacterial action.

Standardization of Sodium Thiosulfate Solution. An oxidizing agent, which will liberate its equivalent of iodine when added to an acid solution of potassium iodide, should be used. Among those suitable are the following primary standards: potassium bichromate, potassium iodate, potassium bromate, copper, and iodine. It is rather difficult to obtain and weigh the iodine in a pure, dry condition. Permanganate solution standardized against sodium oxalate may serve as a secondary standard. Potassium bichromate is readily obtained pure; its only disadvantages are the green color formed when it is reduced to a chromic salt and the oxygen error that occurs when the acidity is sufficient for the reaction to go to completion. Potassium iodate is free from these two disadvantages. It is completely reduced even in acetic acid solution. Copper is a desirable primary standard if the thiosulfate solution is to be used for the determination of this metal.

Standardization against Potassium Bichromate. In this case the reaction is carried out in a solution 0.2-0.4 *N* in hydrochloric acid and containing 4 per cent of potassium iodide. Before titration the solution is diluted until the acidity is not over 0.1 *N*.[1]

Place 4 g. of potassium iodide and 2 g. of sodium bicarbonate (to furnish carbon dioxide to expel oxygen from the flask) in a 500 ml. conical flask, and add 100 ml. of water, recently boiled to remove oxygen and cooled to room temperature. When the salts have dissolved, add 5 or 6 ml. of concentrated hydrochloric acid slowly while rotating the liquid to stir it thoroughly. This volume of acid represents an excess of about 3 ml. Note that the bicarbonate is not added for the purpose of neutralizing the solution, which must be strongly acid for the reaction between bichromate and iodide. An inert atmosphere could be obtained more efficiently but less conveniently by filling the flask with carbon dioxide from some external source. Keep the flask covered as much as possible. The solution must be perfectly

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[1] See Vosburgh, J. Am. Chem. Soc. **44,** 2120 (1922); Bray and Miller, *ibid* **46,** 2204 (1924); Popoff and Whitman, *ibid.* **47,** 2259 (1925).

colorless. Some specimens of potassium iodide when acidified with hydrochloric acid give a yellow coloration due to free iodine. When this occurs, add 0.1 *N* thiosulfate until the solution is colorless. Run in approximately 45 ml. of 0.1 *N* bichromate, accurately measured, mix the solutions thoroughly and rinse down the sides of the flask with a few ml. of boiled water from the wash bottle in such a way that the water will form a thin layer over the solution. Place a clean stopper in the flask and set it aside in the dark for 5 or 6 minutes to allow the following reaction to go to completion:

$$(2)\quad 6KI + K_2Cr_2O_7 + 14HCl = 8KCl + 2CrCl_3 + 3I_2 + 7H_2O.$$

This reaction is not instantaneous unless the solution is heated, but heating causes a loss of iodine. Cool the solution to prevent any loss of iodine, remove the stopper, rinse it off, and dilute the solution to 300-400 ml., using cold, boiled water. Titrate with thiosulfate, while constantly rotating the liquid so as to mix the solutions instantly (why?), until the dark brownish red color has changed to a light yellowish green (Equation (3)). When the iodine has nearly all disappeared and the color of the solution is approaching a pure green, add about 1 or 2 ml. of starch solution and rinse down the sides of the flask. The color should change to a dark blue or to a greenish blue. One reason the starch must not be added at first is that it would not show the approach of the end-point. This method is adopted in all similar titrations since a little iodine, which causes a light yellow coloration in a solution, produces almost as dark a color with starch as does a large amount of iodine. (What is another reason for not adding the starch sooner?) Continue to add the thiosulfate drop by drop. The dark blue color gradually becomes lighter, then turns to a greenish blue, and finally one drop of thiosulfate changes it to a clear green. The end-point is very sharp in a good light against a white background if the solution is not too concentrated, and therefore too deeply colored. Insert the stopper and shake the solution for an instant, to see if the blue color returns at once (iodine vapor in the flask). If it does, add sufficient thiosulfate to remove any blue color. After the solution has stood for a short time, the color will usually return.

(Why?) The end-point is rather abrupt and some experience is required to recognize the final color change. It is very easy to overstep the end-point because of the suddenness with which the blue color changes to green. In such a case the titration must be discarded. It is not possible to add more of the bichromate and continue the titration, because the excess of the thiosulfate may have been decomposed by the acid and also because the reaction with the bichromate is slow. From the result of the first titration estimate approximately the volume of the thiosulfate required for the next one and approach the end-point more carefully. Repeat the titration until the normalities agree within 2 parts per thousand. In the calculation note that the m.e. of potassium bichromate is 0.049035 g. (see p. 242).

If preferred, individual samples of potassium bichromate of about 0.22 g. each may be substituted for portions of a standard solution. Thus any errors involved in the preparation and measurement of the standard bichromate solution are avoided.

Standardization against Potassium Iodate. This substance has two advantages: it forms a colorless reduction product, and reacts almost instantaneously with iodide in a solution so slightly acid that the error due to the action of oxygen of the air with iodide is negligible. An atmosphere of carbon dioxide is therefore unnecessary. The salt must be specially purified. Its equivalent is one-sixth of the molecular weight so that 3.567 g. of potassium iodate is required for one liter of 0.1 *N* solution. If individual samples are used, weigh into 250 ml. conical flasks about 0.12-0.17 g. of the salt, and dissolve in 50 ml. of water which has been recently boiled. Add 2 g. of potassium iodide to the solution, and as soon as this has dissolved, 1 ml. of concentrated hydrochloric acid diluted to 10 or 15 ml. If a standard iodate solution is used, add approximately 45 ml. portions of a 0.1 *N* solution and the acid to 2 g. samples of potassium iodide which have been dissolved in a small amount of water in 250 ml. conical flasks. The reaction (Equation (25)) is almost instantaneous. Titrate the iodine immediately with the thiosulfate solution. Add starch as indicator when the solution has become a faint yellow. Calculate the normality of the thiosulfate. The m.e. of potassium iodate is 0.03567 g.

Standardization against a Potassium Permanganate Solution.[1] The final acidity of the solution at the end of the titration should be 0.05 to 0.2 *N*, preferably 0.1 *N*; the concentration of potassium iodide, 6 per cent; the time of standing in a dark place before titration of the iodine with thiosulfate, 10 minutes.

Complete details for this method are not given because permanganate is a secondary standard. So many good primary standards are available for the standardization of thiosulfate solutions that it seems superfluous to include an indirect method.

Standardization against Copper. This method is recommended only when the thiosulfate is to be used for the determination of copper. In a weakly acid solution cupric salts react with an iodide to form iodine and insoluble cuprous iodide:

$$(10)\quad 2Cu(C_2H_3O_2)_2 + 4KI = Cu_2I_2 + I_2 + 4KC_2H_3O_2.$$

The iodine is titrated with thiosulfate. In this reaction the equivalent of copper is its atomic weight and the m.e. is, therefore, 0.06357 g.

The cuprous iodide formed in this reaction is usually colored by adsorbed iodo-starch and is not pure white at the end-point. Foote and Vance[2] have shown that if thiocyanate is added just before the end-point, the cuprous iodide is converted into the less soluble thiocyanate which is white because it does not adsorb iodine.

Cut into small pieces some clean, pure, electrolytic copper foil. Weigh out samples of approximately 0.25 g. into 150 ml. beakers, and dissolve in a mixture of 10 ml. of water and 4 ml. of concentrated nitric acid. Evaporate the solution on a low-temperature hot plate or water bath until the excess of acid is removed and the salt solidifies on cooling. Do not carry the evaporation so far that a basic nitrate is formed, because such a salt will not dissolve readily. Dissolve the copper nitrate in about 25 ml. of water and add, drop by drop, 1 *N* sodium hydroxide until a slight permanent precipitate of cupric hydroxide forms. Dissolve this by adding 4 ml. of glacial acetic acid, and dilute with water to 70 ml. To the cool solution add 3 g. of

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[1] Popoff and Whitman, J. Am. Chem. Soc. **47,** 2259 (1925); Bray and Miller, ibid. **46,** 2204 (1924).

[2] H. W. Foote and J. E. Vance, J. Am. Chem. Soc. **57,** 845 (1935); Ind. Eng. Chem. Anal. Ed. **8,** 119 (1936), **9,** 205 (1937).

potassium iodide dissolved in a few ml. of water, allow the mixture to stand for half a minute, and then titrate immediately with thiosulfate until the brown color due to iodine has changed to a light yellow. Add 2 ml. of starch solution and continue the titration, stirring constantly, until the blue color nearly disappears. Add 2 g. of ammonium or potassium thiocyanate and titrate to the complete disappearance of the blue color. The blue color may return after a few minutes but the end-point is marked by its first complete disappearance for five or ten seconds.

Errors. The principal sources of error in the processes just described are the liberation of iodine from iodide by the action of the oxygen in the air, which would cause the normality of the thiosulfate to be low; the possible loss of iodine by volatilization, which would lead to a high value for the normality; and incomplete reduction of the oxidizing agent (see p. 263), which would cause the normality to be high.

Other Applications. It is evident that these processes for standardizing a thiosulfate solution may be reversed and used for the determination of iodate, permanganate, chromium, and copper. Essentially the same procedure is used in determining the other oxidizing agents (p. 262), the principal variation being in the concentration of acid, which must sometimes be very high, as in the case of an arsenate, or may sometimes be quite low, as with an iodate. The reaction with ferric ion is very slow. Detailed procedures will be given for the determination of hypochlorite in bleaching powder and of copper in an ore.

Two equations are always required to describe the volumetric determination of oxidizing substances by this method: one in which free iodine is liberated, and one in which the iodine is titrated with standard thiosulfate.

DETERMINATION OF THE AVAILABLE CHLORINE IN BLEACHING POWDER

Bleaching powder, or chloride of lime, consists mainly of a calcium salt, which is a derivative both of hydrochloric and hypochlorous acids, and has the formula $CaClOCl$. The active ingredient is hypochlorite, and it is customary to express the value of bleaching powder in terms of "available chlorine" which refers to the percentage of chlorine liberated when the powder is treated with an acid:

(11) $CaCl_2O + 2HCl = CaCl_2 + Cl_2 + H_2O$.

Pure hypochlorous acid reacts in a similar manner

(12) $HClO + HCl = Cl_2 + H_2O$.

The amount of available chlorine may be determined in either of two ways: 1. Standard thiosulfate solution may be used to titrate the iodine liberated by the action of hypochlorite with an excess of iodide in an acid solution:

(13) $CaCl_2O + 2KI + 2HCl = CaCl_2 + 2KCl + I_2 + H_2O$.

2. The hypochlorite may be reduced to chloride by standard arsenite solution:

(14) $CaCl_2O + NaAsO_2 + 2NaOH = CaCl_2 + Na_3AsO_4 + H_2O$.

The end-point in this reaction is determined by noting the point at which a drop of the solution, when brought into contact with starch-iodide paper, no longer turns the latter blue.

Thiosulfate Method. *Procedure.* Weigh accurately a 5 g. sample of the bleaching powder and rub it in a mortar with successive portions of water until it is thoroughly ground. Wash the contents into a 500 ml. volumetric flask, dilute to the mark with water, and shake the mixture until the bleaching powder is thoroughly in suspension. Unless triturated to a fine powder, lumps will inclose hypochlorite. Transfer a 50 ml. portion of this freshly prepared, homogeneous suspension with a pipette to a 250 ml. conical flask. Dilute the sample to 100 ml., add 2 g. of potassium iodide and 15 ml. of glacial acetic acid. Titrate the iodine liberated with 0.1 *N* thiosulfate. Add 2 ml. of starch solution as indicator just before the yellow color in the solution disappears.

The percentage of available chlorine is calculated from the average value of duplicate analyses which should agree closely. Note that the m.e. of chlorine is 0.03546 and that only one-tenth of the original sample was titrated.

Arsenite Method. *Procedure.* Proceed as in the method just described, but transfer the 50 ml. sample of the suspension to a

250 ml. beaker. Titrate with 0.1 *N* arsenite solution until no blue color develops when starch-iodide paper is touched by a drop of the solution. Prepare the test paper by dipping strips of filter paper into a starch solution containing a little potassium iodide (p. 265). Drain these strips and spread them upon a watch glass to dry.

Prepare a 0.1 *N* sodium arsenite solution by dissolving 4.9455 g. of pure, dried arsenious oxide in a solution of 10 g. of sodium hydroxide in 30 ml. of water. The oxide dissolves readily when the solution is warmed. Dilute the solution in a 1000 ml. volumetric flask to about 500 ml., and neutralize it by adding 21 ml. of concentrated hydrochloric acid, followed by 10 g. of sodium bicarbonate. Then dilute the solution accurately to one liter and mix it thoroughly.

DETERMINATION OF COPPER IN AN ORE

An iodometric method for pure copper has already been described. Iron, arsenic, and antimony may also be present with copper in ores, and these metals in their higher states of oxidation will liberate iodine from an iodide. Iron may be converted into the complex ferric fluoride, FeF_6^{---}, in which the concentration of ferric ion is so low that it has no oxidizing action on an iodide. Arsenic and antimonic compounds will not oxidize an iodide in a solution having a *p*H of 3.5 or more, whereas the reduction of cupric ion is complete even in a solution of *p*H 5.5. To meet such cases Park[1] has described a rapid method for the determination of copper in ores, based on a careful study of the various factors involved. His method, as modified by Crowell, and by Foote and Vance,[2] the procedure of which follows, is much shorter than any in which copper is separated from interfering metals.

Procedure. Heat a 0.5 to 1 g. sample of the finely ground ore with nitric acid until all the copper has dissolved. Concentrate the solution to about 5 ml., add 30 ml. of water and boil the material to be assured of complete solution of soluble matter and also to expel oxides of nitrogen. Filter and wash the residue

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[1] B. Park, Ind. Eng. Chem. Anal. Ed. **3**, 77 (1931).

[2] W. R. Crowell, et al., Ind. Eng. Chem. Anal. Ed. **8**, 9 (1936); H. W. Foote and J. E. Vance, ibid. **8**, 119 (1936); **9**, 205 (1937).

carefully with hot, dilute nitric acid. If the residue is small in amount, or light in color, filtration may be omitted. Concentrate the solution to about 30 ml.; when it is cool, add ammonia until the iron is completely precipitated and the solution smells distinctly of ammonia. Avoid an excess of ammonia. While stirring the mixture constantly, add 2 g. of ammonium bifluoride, NH_4HF_2, weighed to within 0.1 g., and 3 g. of potassium iodide; continue stirring until all the salts have dissolved. The solution will have a *p*H of approximately 3.5. Titrate it at once with 0.1 *N* thiosulfate, and when near the end-point add 2 ml. of starch solution as indicator. When the blue color becomes faint add 2 or 3 g. of ammonium thiocyanate and complete the titration. After the end-point is reached, the blue color should not return within 15 minutes. A quick return of the color may be caused by insufficient fluoride. One gram of this salt should be added for each 0.1 g. of iron or aluminum; the accuracy of the method decreases as the amount of iron increases. If the *p*H of the solution is too high, the reaction between cupric and iodide ions will be slow and the end-point may not be permanent.

According to Caldwell[1] the end-point in the absence of thiocyanate is improved by adding a protective colloid, 0.5 to 1 ml. of a 4 per cent alcoholic solution of white shellac when most of the iodine has been titrated. This flocculates the cuprous iodide and deactivates the surface so that further adsorption is reduced.

If the copper is not entirely dissolved by treatment of the ore with nitric acid, some other method must be used. Ten ml. of bromine water should be added before reduction of the cupric ion to oxidize any arsenic and antimony, and the solution should be boiled until all bromine is removed. Such a condition may exist if the ore was dissolved in nitric and hydrochloric acids, and the solution evaporated with sulfuric acid to fumes of the latter. Any sulfur present would then have reduced arsenic and antimony to the trivalent form. Calculate the percentage of copper in the ore. The m.e. of copper is 0.06357 g.

It is often preferred to separate the copper from iron by precipitating the former as metal or sulfide. Zinc or aluminum is added and any traces of copper left in solution are precipitated by hydrogen sulfide. The combined copper and sulfide precipitate is dissolved in nitric acid, the solution filtered and any

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[1] Caldwell, J. Am. Chem. Soc. **57**. 96 (1935).

arsenic and antimony oxidized with bromine water. The excess of bromine is removed by boiling, the solution is made alkaline with ammonia, then acidified with acetic acid, after which potassium iodide is added and the titration performed as already described.

Standard Iodine. Iodine is only slightly soluble in water but the solubility is considerably increased by the presence of potassium iodide, due probably to the formation of an unstable periodide, KI_3. The more concentrated a potassium iodide solution, the more readily is iodine dissolved in it, and although the latter dissolves very slowly in dilute potassium iodide a concentrated solution of the periodide may be considerably diluted without separation of solid iodine. Since it is rather difficult to obtain iodine in pure and dry form, a standard solution of it is not prepared directly. Moreover, iodine has an appreciable vapor pressure and therefore tends to escape whenever a bottle containing the solution of it is opened. An iodine solution is stable if kept sealed in the dark and if made from pure reagents.

Preparation and Standardization of 0.1 *N* Iodine Solution. From the equation

$$(15)\quad I_2 + 2e \rightleftharpoons 2I^-$$

it is evident that the oxidation number of iodine changes from 0 to − 1. Accordingly, the equivalent of the element is its atomic weight, 126.92, and one liter of 0.1 *N* solution contains 12.692 g. Twenty to twenty-four grams of potassium iodide is the quantity required to keep this amount of iodine in solution. Since both iodine and potassium iodide are rather expensive, only 500 ml. of solution should be used for the work on arsenious oxide.

Weigh out on the side-table balance (never on an analytical balance on account of iodine vapor) 6.5 g. of pure iodine, place it in a 150 ml. beaker, add 10-11 g. of potassium iodide and 20 ml. of water. Stir the mixture occasionally until the iodine is dissolved but do not heat. (Why?) Dilute the solution to 500 ml. in a flask or cylinder; look carefully for any undissolved particles of iodine; if any are apparent the solution must be filtered. Transfer the liquid to a dry, glass-stoppered bottle. Store the solution in a locker away from light, which accelerates the oxidation of the iodide to iodine.

The thiosulfate which has already been standardized may be used in standardizing the iodine (Equation (3)). Draw off approximately 45 ml. of iodine into a 250 ml. conical flask, dilute to 100 ml., add 1 ml. of glacial acetic acid, and run in the thiosulfate solution until the yellow color becomes faint. Then add 2 ml. of starch solution as indicator, and continue the titration until the blue color just disappears. A good end-point can be obtained without any indicator in bright light against a white background. If the end-point is overstepped, titrate back with iodine. Sometimes it is more satisfactory to titrate to the appearance of the blue color rather than to its disappearance. Repeat the titration until satisfactory agreement is obtained. (2-3 parts per thousand parts.)

The ml. of the thiosulfate used should be multiplied by the normality of the solution to obtain the equivalent volume of a normal thiosulfate solution. This last volume is then divided by the volume of iodine solution to obtain the normality of the latter.

It is advisable to standardize the thiosulfate and the iodine and to titrate the arsenious oxide sample within as short a period of time as possible, in order to eliminate errors resulting from possible changes in the concentration of the solutions.

The most precise method of standardizing an iodine solution is against pure arsenious oxide, As_2O_3.[1] This primary standard of guaranteed purity may be obtained from the National Bureau of Standards. It may also be purchased in a very pure form from dealers, or it may be purified by crystallization from hydrochloric acid followed by sublimation. In such a standardization the arsenious oxide is treated as described in the next section, "Determination of Arsenic in Arsenious Oxide." This method of standardization is more exact than the one used above, since no other standard solution is involved.

DETERMINATION OF ARSENIC IN ARSENIOUS OXIDE. IODINE TITRATION METHOD

Principle. The arsenious oxide is dissolved in sodium carbonate or sodium hydroxide; sodium arsenite is formed:

(16) $As_2O_3 + Na_2CO_3 = 2NaAsO_2 + CO_2$.

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[1] Chapin, J. Am. Chem. Soc. **41**, 351 (1919).

The solution is acidified to remove any sodium hydroxide or carbonate. More than enough acid to form sodium bicarbonate is required. Solid sodium bicarbonate in excess is then added to neutralize the acid. Thus a solution containing sodium bicarbonate and saturated with carbon dioxide is formed which acts, therefore, as a buffer solution. The arsenite present is largely in the form of $NaAsO_2$. Such a buffer solution is neutral, and does not of itself react with iodine. An excess of sodium bicarbonate in the solution is essential to prevent the hydriodic acid, formed during the titration, from decreasing the *p*H. To obtain complete oxidation of the arsenite and to avoid the reaction between iodine and hydroxyl ion, the *p*H of the solution must be between 4 and 9,[1] the best value being 6.5, which is very close to the neutral point. In a 0.12 *N* solution of sodium bicarbonate saturated with carbon dioxide, the *p*H is 7; in a solution saturated both with borax and boric acid it is 6.2; in a solution containing two molecules of Na_2HPO_4 to one of NaH_2PO_4 it is about 7. All of these solutions are therefore satisfactory. If the solution is alkaline, some of the iodine will form iodide and iodate (Equations (4) and (5)); if too acid, the reaction with arsenite will not go to completion.

As previously stated (p. 213) it is possible by the addition of mercuric chloride to reduce the concentration of I^- and thus increase the oxidation potential of this system sufficiently to allow complete oxidation of arsenite in an acid solution.[2]

The arsenite is then titrated with standard iodine, and starch is used as indicator:

$$(17)\quad NaAsO_2 + I_2 + 3NaHCO_3 = Na_2HAsO_4 + 2NaI + 3CO_2 + H_2O.$$

The end-point is very sharp under proper conditions and this method therefore gives very accurate results. The reaction:

$$(18)\quad H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2HI$$

may be made to go to completion in either direction according to conditions, and serves thus to determine arsenic in either form. The course of the reaction is from left to right in a neutral solution, and iodine is used as the standard solution; the course

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[1] Washburn, J. Am. Chem. Soc. **30**, 31 (1908).

[2] The color of iodine is used as the indicator since mercuric ion interferes with starch indicator.

is from right to left in the presence of fairly concentrated hydrochloric acid, and thiosulfate is used as the standard solution to titrate the iodine liberated.

Errors. Too much iodine will be used if the solution being titrated is slightly alkaline because of the presence of some normal carbonate or because of a lack of carbon dioxide. (Why?) This point may be illustrated by leaving exposed to the air a solution which has been titrated. Carbon dioxide escapes, the solution becomes alkaline, and the blue color disappears. This error is especially noticeable if the solution is warm. This titration should be performed in a flask and never in a beaker, and the solution should be cool.

If the solution is slightly acid, due to the lack of bicarbonate, the reaction will stop before all the arsenite is oxidized, and the end-point reaction will be slow.

An iodine solution may vary in concentration. It may lose iodine by volatilization, or, if slightly acid, may gain iodine by oxidation, caused by the presence of catalytic impurities which accelerate the action of oxygen.

Other Applications. If antimonyl tartrate preparations[1] are to be analyzed antimony is titrated in the same way, the reaction being reversible as in the case of arsenic. In other compounds to prevent the precipitation of antimonous hydroxide some tartrate is added, which forms, with the antimony, a soluble complex salt, potassium antimonyl tartrate, $K(SbO)C_4H_4O_6$:

$$(19)\quad SbCl_3 + KHC_4H_4O_6 + 3NaHCO_3 = K(SbO)C_4H_4O_6 + 3NaCl + 3CO_2 + 2H_2O.$$

$$(20)\quad K(SbO)C_4H_4O_6 + 4NaHCO_3 + I_2 = NaH_2SbO_4 + 2NaI + KNaC_4H_4O_6 + H_2O + 4CO_2.$$

Sulfurous acid, hydrogen sulfide, and stannous chloride are titrated in an acid solution only. To prevent the escape of hydrogen sulfide, an excess of standard iodine may be added and the excess titrated with standard thiosulfate. The iodometric method is very important in the determination of sulfur in sulfides. It is widely used to determine sulfur in iron and steel. The hydrogen sulfide is often evolved by the action of hydro-

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[1] A brief procedure for soluble antimonyl tartrate preparations is given on p. 281.

chloric acid on the sulfide and is absorbed in sodium hydroxide. The alkali is then acidified and the hydrogen sulfide titrated. Hydrogen sulfide may be absorbed in an ammoniacal solution of cadmium or zinc. The cadmium or zinc sulfide is treated with hydrochloric acid and the hydrogen sulfide titrated with standard iodine, thus:

(21) $\downarrow CdS + 2HCl = CdCl_2 + H_2S.$
(22) $H_2S + I_2 = 2HI + S.$

Tin, when determined, must first be reduced to stannous chloride. Either nickel, lead, iron, antimony, or a mixture of iron and antimony is ordinarily used:

(23) $SnCl_4 + Fe = SnCl_2 + FeCl_2$ or
$SnCl_4 + Pb = SnCl_2 + PbCl_2.$

Many indirect iodometric methods are possible. For example, zinc may be precipitated as zinc sulfide and the latter titrated as described above, although this process is not applicable to most sulfides.

The method described for the determination of arsenic may be reversed and used for the titration of free iodine and certain other oxidizing agents. The preparation of the standard sodium arsenite required for such determinations has already been described, p. 273.

Procedure.[1] Weigh out three samples of 0.3 to 0.4 g. each dried not more than 2 hours (see p. 20) into 250 ml. conical flasks. Add 1 g. of sodium carbonate and 15 ml. of water, and rinse down the sides of the flask. Heat the material just to boiling and keep it hot until the sample dissolves (Equation (16)). Ten or 15 minutes may be required, since arsenious oxide is not easily wet by the solution. Be sure that there are no undissolved particles of the sample on the walls of the flask. Sometimes a slight siliceous residue will remain. Sodium hydroxide, which is often used to dissolve arsenious oxide, is more rapid in its action, but if a little iron is present it tends to cause oxidation of the arsenite by the oxygen in the air; the

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[1] The first part of this procedure is not applicable to soluble antimonyl tartrate mixtures. See p. 281.

sodium hydroxide solution should never be boiled. Dilute the solution to 100 ml., and cool with running water. Add 2 ml. of concentrated hydrochloric acid to neutralize the carbonate, and then add 10 g. of sodium bicarbonate to buffer the solution. There must be an excess of the latter present to keep the solution neutral. (Why?) Stopper the flask until the titration is begun, to prevent the escape of carbon dioxide. (Why?)

Add 2 ml. of starch solution and run in 0.1 N iodine until a faint pink, lavender, or blue tint is obtained, which persists for at least half a minute. The color varies with the kind of starch used, the acidity of the solution, the amount of iodide present, and perhaps other factors. If the solution is cold and the flask closed, the color will usually last for several minutes; otherwise carbon dioxide escapes and the color disappears. (Why?) Be careful not to overstep the end-point. Such a possibility can be avoided by placing in the solution at the beginning of the titration a clean glass tube, 3 or 4 mm. in diameter, and of sufficient length to reach to the neck of the flask. The titration is then carried out as usual until the end-point is reached or slightly over-stepped. The solution within the tube will not have been mixed with the remainder, and may now be utilized by removing and rinsing the tube. If the end-point is slightly overstepped, the excess of iodine may be titrated with standard thiosulfate. From the result of the first titration estimate approximately the volume of iodine required for the next one, and approach the end-point carefully. The device mentioned above has no particular advantage in a second titration.

If preferred, samples of 1.5 to 2 g. may be used instead of individual samples. Dissolve such a sample in 2 g. of sodium carbonate or sodium hydroxide and 20 ml. of water, and transfer the solution to a 250 ml. volumetric flask. Add 3 ml. of concentrated hydrochloric acid and dilute the solution to the mark. Measure out 45 to 50 ml. portions for each titration and add 5 g. of sodium bicarbonate. Dilute the solution to 100 ml. and titrate as above. The first method avoids the error involved in measuring out aliquot portions.

Calculation of Results. According to the equation:

$$(24) \quad As_2O_3 + O_2 = As_2O_5$$

each molecule of arsenious oxide requires 4 equivalents of oxygen;

therefore, the equivalent is $\frac{As_2O_3}{4}$, or 49.45 g. The equivalent of arsenic is then $\frac{As}{2}$, or 37.45 g., and the m.e., 0.03745 g.

Procedure. *Applicable to Soluble Antimonyl Tartrate Preparations.* Weigh accurately 1 g. samples of the undried mixture into 250 ml. conical flasks. Dissolve each sample in 100 ml. of water, adding 2 g. of sodium-potassium tartrate to each solution if a precipitate forms. To the clear solution add 2 g. of sodium bicarbonate and stir or swirl until the solutions are uniform. Add to each flask 2 ml. of starch indicator and titrate as described in the procedure for arsenious oxide, p. 280. From the data calculate and report the per cent of antimony. The method of calculation is exactly analogous to that which has been given for arsenic, p. 280.

PROCESSES INVOLVING STRONGER OXIDIZING AGENTS

Iodate and Bromate. The use of potassium iodate as a primary oxidation standard has already been mentioned. Iodate and iodide do not react in neutral solution, but do react even in a very slightly acid solution with the liberation of one atom of iodine for each equivalent of acid. Because of this reaction it is possible to use an iodometric method for determining free acids or acids in combination with very weak bases as in aluminum chloride. The liberated iodine is titrated with thiosulfate. An excess of iodine-iodate mixture must be present, and in this mixture there must be an excess of iodide.

The following equations also show a method for determining iodate:

(25) $KIO_3 + 5KI \text{ (excess)} + 6HCl = 6KCl + 3I_2 + 3H_2O$.
(26) $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$.

In a fairly concentrated hydrochloric acid solution, iodate is a very much stronger oxidizing agent; it oxidizes iodide not only to iodine but also to iodine chloride, ICl, and is itself reduced to the latter. The first reaction, when iodide is titrated with iodate under these conditions, is the liberation of iodine as in Equation (25). This is then further oxidized:

(27) $2I_2 + KIO_3 + 6HCl = KCl + 5ICl + 3H_2O$.

Both iodine and iodine chloride are brownish yellow in aqueous solution, but in organic solvents, such as chloroform and carbon tetrachloride, iodine is purple, while iodine chloride remains yellow. The point at which the last trace of iodine disappears may be determined by the change in color from purple to yellow of a drop of chloroform shaken up in the solution during the titration. The equivalent of the iodate in this reaction is found by the equation:

$$(28)\quad IO_3^- + Cl^- + 6H^+ + 4e = ICl + 3H_2O$$

from which it is evident the equivalent is $\frac{KIO_3}{4}$. This reaction is also extensively used for titrating a thiocyanate (especially cuprous thiocyanate):

$$(29)\quad 4CuCNS + 7KIO_3 + 14HCl = 4HCN + 4CuSO_4 + 7ICl + 7KCl + 5H_2O;$$

also for titrating trivalent arsenic and antimony, mercurous chloride, etc. All of these methods are described by Jamieson.[1]

Potassium bromate in a solution containing considerable hydrochloric acid is a very strong oxidizing agent. Bromate is used principally for the titration of trivalent arsenic and antimony:

$$(30)\quad 3HAsO_2 + KBrO_3 + 3H_2O(+ HCl) = 3H_3AsO_4 + KBr.$$

$$(31)\quad 3HSbO_2 + KBrO_3 + 3H_2O(+ HCl) = 3H_3SbO_4 + KBr.$$

Some suitable organic dye is added as an indicator, usually methyl red or methyl orange. The dye is bleached by the bromine formed by the action of the first slight excess of bromate with the bromide in solution:

$$(32)\quad KBrO_3 + 5KBr + 6HCl = 6KCl + 3Br_2 + 3H_2O.$$

Other indicators, some of which appear to be more efficient than the two mentioned, have been suggested[2] for these titrations. This method is one of the best for arsenic and antimony.

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[1] Jamieson, Volumetric Iodate Methods. The Chemical Catalog Co., New York, 1926.

[2] Smith and Bliss, J. Am. Chem. Soc. **53**, 2091 (1931).

Review Questions and Problems

1. A sample of pure potassium iodate, weighing 0.3050 g. requires 40.10 ml. of thiosulfate solution to titrate the iodine liberated in the presence of excess of iodide. What is the normality of the solution?

2. In the iodometric determination of copper in an ore containing arsenic and iron what is the purpose of adding fluoride and of maintaining a pH of not less than 3.5?

3. Explain on the basis of oxidation-reduction potentials three possible methods of causing a direct iodometric titration to go farther towards completion and give an example of each.

4. Explain the theoretical basis for four methods that might be used to cause an indirect iodometric reaction to go farther towards completion and illustrate by examples.

5. Explain why buffers in the neutral range are sometimes necessary in direct iodometric titrations and give three which are useful in maintaining a pH about 7.

6. To 1.0000 g. of a sample containing potassium sulfate and bisulfate is added excess of a neutral mixture of iodide and iodate containing excess of iodide. The iodine liberated requires 40.00 ml. of 0.1200 N thiosulfate. Calculate the percentage of potassium bisulfate in the sample.

7. Ammonium salts are oxidized to nitrogen by hypochlorite. Calculate the percentage of nitrogen in a sample weighing 1.0600 g. to which 40.10 ml. of 0.1080 N hypochlorite has been added and which requires 10.80 ml. of 0.1100 N thiosulfate for titration of the excess after adding potassium iodide.

8. In the use of potassium bromate as an oxidizing agent explain what difference you would expect between its action in a solution containing mercuric sulfate and in a solution free from mercury.

9. A solution of potassium iodate contains ⅙ of a molecular weight in grams per liter. It is used in titrating cuprous thiocyanate (Equation (29)) and 70.00 ml. is required for a sample weighing 1.0000 g. Calculate the percentage of copper in the sample.

Ans. 42.38 per cent.

10. A certain weight of CrO_3 is ignited to Cr_2O_3, losing 0.2400 g. Assuming that the loss is all oxygen, what volume of normal ferrous sulfate would have been required to titrate it?

Note.—Do not calculate the weight of either oxide.

11. The mercury in a 1.0000 g. sample is precipitated as the periodate, $Hg_5(IO_6)_2$, and dissolved in excess of hydrochloric acid and potassium iodide forming K_2HgI_4 and iodine. The iodine requires for titration 32.00 ml. of 0.1000 N thiosulfate. Calculate the percentage of mercury in the sample.

Ans. 20.06 per cent.

Suggestion: Write the equation for the reduction of the periodate.

12. The sulfur in a 5.00 g. sample of steel containing 0.12 per cent sulfur requires 15.30 ml. of an iodine solution. The same weight of a

sample containing 0.05 per cent sulfur requires 6.55 ml. What amount of solution represents the "blank" required to show the end-point?

13. Explain how arsenic and arsenious acids can each be determined iodometrically when present together. Define rather closely the conditions for each determination.

14. The arsenic in a 1.0000 g. sample is reduced to metallic arsenic, which is dissolved in a neutral solution containing 100.00 ml. of 0.2000 *N* iodine. The excess of the latter requires 8.00 ml. of 0.2500 *N* thiosulfate. Calculate the percentage of arsenic in the sample.

15. A certain weight of oxalic acid is converted into water, carbon dioxide and carbon monoxide. The latter reacts with iodine pentoxide thus: $I_2O_5 + 5CO = I_2 + 5CO_2$. The iodine liberated requires 30.00 ml. of 0.1000 *N* thiosulfate. What weight of oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, was present?

Ans. 0.9454 g.

16. In a sample of alloy weighing 1.0350 g. the tin was reduced to stannous chloride, which required 40.15 ml. of 0.1155 *N* iodine for titration. Calculate the percentage of tin in the alloy.

17. The sulfur in 3.000 g. of steel was evolved as hydrogen sulfide and absorbed in 50.00 ml. of 0.0100 *N* hypochlorite solution, which oxidized it to sulfate. The excess of hypochlorite required 7.50 ml. of 0.0200 *N* thiosulfate after the addition of acid and potassium iodide. Calculate the percentage of sulfur in the steel.

Ans. 0.0467 per cent.

18. Ten g. of a solution containing only iodic acid, sulfuric acid and water requires 35.00 ml. of normal alkali for neutralization. The same weight requires 48.00 ml. of normal thiosulfate to titrate the iodic acid. Calculate the percentage of each acid in the solution.

19. Calculate the error in the iodometric determination of the percentage of bromine in bromine water caused by the failure to know that 0.293 per cent of iodic acid was present which also liberated iodine from potassium iodide.

20. Ten g. of a solution containing only thiocyanic acid, oxalic acid and water requires 20.00 ml. of normal alkali to neutralize both acids and 45.00 ml. of normal oxidizing agent to oxidize both acids, the thiocyanic acid forming $HCN + H_2SO_4$. Calculate the percentage of each anhydrous acid present.

Ans. 2.954 per cent HCNS, 6.751 per cent $H_2C_2O_4$.

21. In standardizing thiosulfate, 0.2450 g. of pure potassium bichromate requires 45.52 ml. of thiosulfate. Calculate the normality of the solution.

22. Name as many standard oxidizing solutions as possible that can be used for the titration both of trivalent arsenic and antimony. Write equations for the reaction of three of these oxidizing agents with either arsenic or antimony.

23. A sample of pure arsenious oxide weighing 0.1575 g. requires 40.12 ml. of standard iodine solution. Calculate the normality of the solution.

SUMMARY OF VOLUMETRIC REACTIONS

The following volumetric determinations have been studied. The student should be able to balance the equations for the following reactions:

Silver

$AgNO_3+KCNS =$

(Indicator) $Fe(NO_3)_3+KCNS =$

Lead

$PbSO_4+NH_4C_2H_3O_2 =$

(*a*) $Pb(C_2H_3O_2)_2+Na_2MoO_4 =$

(*b*) $Pb(C_2H_3O_2)_2+K_2Cr_2O_7+H_2O =$

$PbCrO_4+HCl+FeSO_4 =$

Copper

(*a*) $CuSO_4+KI =$

(*b*) $CuSO_4+NH_4CNS+H_2SO_3+H_2O =$

$CuCNS+HIO_3+HCl =$

$CuCNS+KMnO_4+H_2SO_4 =$

(*c*) $(NH_3)_4Cu(NO_3)_2+KCN+H_2O =$

Arsenic

(*a*) $NaAsO_2+NaHCO_3+I_2 =$

(*b*) $HAsO_2+KBrO_3(+HCl) =$

(*c*) $HAsO_2+KIO_3+HCl$ (conc.) $=$

(*d*) $H_3AsO_4+KI+HCl =$

(*e*) $HAsO_2+Ce(SO_4)_2+H_2O =$

Chromium

$Cr_2(SO_4)_3+(NH_4)_2S_2O_8(+AgNO_3) +H_2O =$

or $Cr_2(SO_4)_3+KMnO_4+H_2O =$

$H_2CrO_4+FeSO_4+H_2SO_4 =$

(Abs. of Fe) $K_2Cr_2O_7+KI+HCl =$

Manganese

(*a*) $Mn(NO_3)_2+NaBiO_3+HNO_3 =$

$HMnO_4+FeSO_4+H_2SO_4 =$

(*b*) $MnSO_4+(NH_4)_2S_2O_8(+AgNO_3) =$

$HMnO_4+H_2O_2+H_2SO_4 =$

(*c*) $MnCl_2+KMnO_4+ZnO =$

Zinc

$ZnCl_2+K_4Fe(CN)_6 =$

(end pt.) $UO_2SO_4+K_4Fe(CN)_6 =$

Nickel

$NiCl_2+NH_4OH =$

$Ni(NH_3)_4Cl_2+KCN =$

(end pt.) $AgI+KCN =$

Antimony

(*a*) $NaSbO_2+NaHCO_3+NaHC_4H_4O_6+I_2 =$

(*b*) $SbCl_3+KBrO_3+HCl =$

(*c*) $SbCl_3+KMnO_4+HCl =$

(*d*) $SbCl_3+KIO_3+HCl$ (conc.) $=$

(*e*) $H_3SbO_4+KI(+HCl) =$

Tin

$SnCl_4+Ni$ or Pb or $Fe =$

$SnCl_2+I_2+HCl =$

Iron

(*a*) $Fe_2(SO_4)_3+Al$ or Zn or $Cd =$

(*b*) $Fe_2(SO_4)_3+H_2SO_3+H_2O =$

(*c*) $FeSO_4+KMnO_4+H_2SO_4 =$

(*d*) $FeCl_3+SnCl_2 =$

$SnCl_2+HgCl_2 =$

$FeCl_2+K_2Cr_2O_7+HCl =$

$FeCl_2+Ce(SO_4)_2 =$

Calcium

$CaCl_2+(NH_4)_2C_2O_4 =$

$CaC_2O_4+H_2SO_4+KMnO_4 =$

Chlorine

$Cl_2+KI =$

$NaCl+AgNO_3 =$

$$\left.\begin{matrix}NaClO\\ NaClO_2\\ NaClO_3\end{matrix}\right\}+KI+HCl =$$

$I_2+NaS_2O_3 =$

$NaClO_3+FeSO_4$ (excess) $=$

$NaClO+Na_3AsO_3 =$

Bromine

Same as above, but no $NaBrO_2$ is known.

$FeSO_4$ not used for $NaBrO_3$.

Iodine

$KI + AgNO_3 =$

$KIO_3 + KI + HCl$ (dilute) $=$

$I_2 + Na_2S_2O_3 =$

$KI + HIO_3 + HCl$ (conc.) $=$

$KI + KMnO_4$ (excess) $+ H_2O =$

Sulfur

$H_2S + I_2 =$

$Na_2S_2O_3 + I_2 =$

$H_2SO_3 + I_2 + H_2O =$

$H_2S_2O_8 + KI =$

$K_2S_2O_8 + FeSO_4$ (excess) $=$

Miscellaneous

$H_2O_2 + Ce(SO_4)_2 =$

$H_2O_2 + KMnO_4 + H_2SO_4 =$

$H_2O_2 + KI + HCl =$

$KNO_2 + KI + HCl =$

$KNO_2 + KMnO_4 + H_2SO_4 =$

$HCNS + AgNO_3 =$

$HCNS + HIO_3 + HCl =$

$HCNS + KMnO_4 + H_2SO_4 =$

$NaCN + AgNO_3 =$

$NaAg(CN)_2 + AgNO_3 + KI + NH_4OH =$

$H_2C_2O_4 + Ce(SO_4)_2 =$

$H_2C_2O_4 + KMnO_4 + H_2SO_4 =$

$K_4Fe(CN)_6 + KMnO_4 + H_2SO_4 =$

$H_4Fe(CN)_6 + Ce(SO_4)_2 =$

$K_3Fe(CN)_6 + KI + HCl =$

$MnO_2 + FeSO_4 + H_2SO_4 =$

$MnO_2 + HCl =$

$PbO_2 + HCl =$

$Na_2CO_3 + HCl$ (m. o.) $=$

$Na_2CO_3 + HCl$ (ph. th.) $=$

Equations illustrating the use of the principal standard solutions. Complete and balance:

Sodium Hydroxide

(1) $NaOH + H_3PO_4$ (m.o.) $=$

(2) $NaOH + H_3PO_4$ (ph. th.) $=$

Hydrochloric Acid

(3) $HCl + Na_2CO_3$ (m. o.) $=$

(4) $HCl + Na_2CO_3$ (ph. th.) $=$

(5) $HCl + Na_2B_4O_7 + H_2O =$

Potassium Permanganate

(6) $KMnO_4 + FeSO_4 + H_2SO_4 =$

(7) $KMnO_4 + MnSO_4 + ZnO =$

(8) $KMnO_4 + HAsO_2 + HCl =$

(9) $KMnO_4 + HSbO_2 + HCl =$

(10) $KMnO_4 + KNO_2 + H_2SO_4 =$

(11) $KMnO_4 + KI + H_2O =$

(12) $KMnO_4 + HCNS + H_2SO_4 =$

(13) $KMnO_4 + H_4Fe(CN)_6 + H_2SO_4 =$

(14) $KMnO_4 + H_2C_2O_4 + H_2SO_4 =$

(15) $KMnO_4 + H_2O_2 + H_2SO_4 =$

Potassium Bichromate

(16) $K_2Cr_2O_7 + FeSO_4 + H_2SO_4 =$

(17) $K_2Cr_2O_7 + FeCl_2 + HCl =$

(18) (e.p.) $FeSO_4 + K_3Fe(CN)_6 =$

Ferrous Sulfate

(19) $FeSO_4 + Ce(SO_4)_2 =$

(20) $FeSO_4 + HMnO_4 + H_2SO_4 =$

(21) $FeSO_4 + MnO_2 + H_2SO_4 =$

(22) $FeSO_4 + H_2CrO_4 + H_2SO_4 =$

(23) $FeSO_4 + K_2S_2O_8 =$

(24) $FeSO_4 + KClO_3 + H_2SO_4 =$

Iodine

(25) $I_2 + H_2S =$

(26) $I_2 + H_2SO_3 + H_2O =$

(27) $I_2 + Na_2S_2O_3 =$

(28) $I_2 + KCN = ICN +$

(29) $I_2 + K_4Fe(CN)_6 =$

(30) $I_2 + NaAsO_2 + NaHCO_3 =$

(31) $I_2 + NaSbO_2 + NaHCO_3 +$
$NaHC_4H_4O_6 =$

(32) $I_2 + SnCl_2 + HCl =$

Sodium Thiosulfate. KI in excess acid soln.

(33) $Na_2S_2O_3 + I_2 =$

(34) $KI + Cl_2 =$

(35) $KI + KClO + HCl =$

(36) $KI + KClO_2 + HCl =$

(37) $KI + KClO_3 + HCl =$

(38) $KI + Br_2 =$

(39) $KI + KBrO_3 + HCl =$

(40) $KI + KIO_3 + HCl =$

m.o. = methyl orange. ph. th. = phenolphthalein. e.p. = end-point.

(41) $KI+K_2S_2O_8 =$
(42) $KI+KMnO_4+HCl =$
(43) $KI+H_2O_2+H_2SO_4 =$
(44) $KI+H_2CrO_4+HCl =$
(45) $KI+H_3AsO_4+HCl =$
(46) $KI+KNO_2+HCl =$
(47) $KI+H_3Fe(CN)_6+HCl =$
(48) $KI+CuSO_4 =$
(49) $KI+H_3SbO_4 =$
(50) $KI+FeCl_3 =$
(51) $KI+MnO_2+HCl =$

POTASSIUM IODATE

(52) $KIO_3+As_2O_3+HCl$ (conc.) =
(53) KIO_3+SbCl_3+HCl (conc.) =
(54) $KIO_3+KI+HCl$ (conc.) =
(55) $KIO_3+CuCNS+HCl$ (conc.) =

POTASSIUM BROMATE

(56) $KBrO_3+HAsO_2(+HCl) =$
(57) $KBrO_3+SbCl_3(+HCl) =$
(58) (e.p.) $KBrO_3+KBr+HCl =$

CERIC SULFATE

(59) $Ce(SO_4)_2+FeSO_4 =$
(60) $Ce(SO_4)_2+H_2C_2O_4 =$
(61) $Ce(SO_4)_2+HAsO_2+H_2O =$
(62) $Ce(SO_4)_2+H_2O_2 =$
(63) $Ce(SO_4)_2+H_4Fe(CN)_6 =$

SILVER NITRATE

(64) $AgNO_3+KCl =$
(65) (e.p.) $AgNO_3+K_2CrO_4 =$
(66) $AgNO_3+KBr =$
(67) $AgNO_3 + KI =$
(68) $AgNO_3+KCNS =$
(69) $AgNO_3+KCN$ (excess) =
(70) (e.p.) $AgNO_3+NaAg(CN)_2+KI$
$+NH_4OH =$

SODIUM CYANIDE

(71) $NaCN+(NH_3)_4NiCl_2 =$
(72) (e.p.) $NaCN+AgI =$
(73) $NaCN+Cu(NH_3)_4(NO_3)_2+H_2O =$

MISCELLANEOUS

(74) $K_4Fe(CN)_6+ZnCl_2 =$
(75) $(NH_4)_2MoO_4+Pb(C_2H_3O_2)_2 =$
(76) $KCNS+AgNO_3 =$
(77) (e.p.) $KCNS+Fe(NO_3)_3 =$

CHAPTER XV

GRAVIMETRIC ANALYSIS

PRECIPITATION. WASHING. IGNITION. CALCULATIONS

The nature of a gravimetric analysis has been explained briefly in Chapter I, p. 3, and the general operations of a complete analysis have been outlined there, pp. 8-9. A study of Chapter II should precede the present one because an introduction to the laboratory work is given as well as a detailed consideration of the general operations: Sampling, solution and filtration, together with a brief treatment of washing and ignition. Weighing is considered in detail in Chapter III. Of the general operations there remain to be considered in detail here: Precipitation, washing and some further points about ignitions. The methods of calculation that are frequently used in this branch of the subject are also outlined. The important topic of quantitative separations is considered in Chapter XVII and electroanalytical separations are dealt with in Chapters XIX and XX.

In gravimetric analysis the element to be considered is separated from a weighed sample of material and weighed as such or in the form of a pure stable compound. If the element is separated by precipitation, the form in which it is precipitated must be so insoluble that no appreciable loss occurs when the precipitate is collected by filtration, washed and subsequently converted by drying or ignition into a substance suitable for weighing. If the precipitate can not be weighed after drying or ignition, due to unsuitable properties, it may be dissolved and converted into a form more suitable for weighing. It is desirable that an element be separated and determined through a single precipitation process, but such a procedure is often impossible. Frequently the precipitate that is best adapted for the separation of an element from other elements can not be satisfactorily ignited and weighed, or the precipitate best suited for ignition and weighing may not afford a satisfactory separation from other elements.

Illustration.. Manganese may be separated in a concentrated nitric acid solution containing chlorate from nearly all elements, in the form of manganese dioxide, MnO_2, but this precipitate is not in a form suitable for ignition and weighing. The element is most satisfactorily weighed in the form of manganese pyrophosphate, $Mn_2P_2O_7$, which is obtained from manganese ammonium phosphate, $MnNH_4PO_4$, by igniting the latter. All elements except the alkali metals interfere in the precipitation of this double ammonium phosphate, so that in the gravimetric determination of manganese it is often necessary first to use some special method to separate the element from materials which would interfere later in the precipitation of manganese ammonium phosphate.

Whenever possible, a form should be chosen which is not only suitable for ignition and weighing, but which gives at the same time a quantitative separation from all other substances that may be present. An extra precipitation and filtration are thereby

TABLE XV. FORMS COMMONLY WEIGHED IN GRAVIMETRIC ANALYSIS

Element	Weighed as	Element	Weighed as
Ag	AgCl	H	H_2O*
Al	Al_2O_3; $AlPO_4$	Hg	Hg; HgS
As	$Mg_2As_2O_7$; As_2S_3	I	AgI
Ba	$BaSO_4$	Mg	$Mg_2P_2O_7$
Bi	Bi_2O_3; $BiPO_4$	Mn	$Mn_2P_2O_7$; Mn_3O_4
Br	AgBr	Ni	Ni; Dimethylglyoxime-nickel; NiO
C	$BaCO_3$; CO_2*	P	$Mg_2P_2O_7$
Ca	$CaCO_3$; CaO	Pb	$PbSO_4$; PbO_2
Cd	Cd; $Cd_2P_2O_7$	S	$BaSO_4$
Cl	AgCl	Sb	Sb_2O_4; Sb_2S_3
Co	Co_3O_4; $CoSO_4$	Si	SiO_2
Cr	Cr_2O_3; $PbCrO_4$	Sn	Sn; SnO_2
Cu	Cu; CuO	Sr	$SrSO_4$
Fe	Fe_2O_3	Zn	$Zn_2P_2O_7$; ZnO

* Carbon dioxide is absorbed in an alkaline reagent, e.g. "ascarite" and the gain in weight is determined. Combined hydrogen is determined by converting it to water and weighing the latter in the form of the gain in weight of a suitable absorbing agent

avoided. Comparatively few compounds of the different metals and non-metals can readily be obtained in a form sufficiently pure to be used in the quantitative determination of these elements. Without considering the various reasons which make other compounds less suitable, Table XV lists the forms in which the common elements are usually weighed.

PRECIPITATION

The majority of gravimetric processes are based upon a separation of the desired element by precipitation, followed by washing and drying or ignition. The precipitation process is made a separation process from all other elements as far as possible. In a precipitation process the following factors are of chief concern: (a) The solubility of the precipitate; (b) The physical character of the precipitate; and (c) The purity of the precipitate. These factors will now be discussed in some detail.

The Solubility of Precipitates. (1) **The Common Ion Effect.** This topic is dealt with extensively in courses in qualitative analysis. The use of a slight excess of the precipitant has a marked influence in diminishing the solubility of a precipitate, as would be expected from the solubility-product principle. In modern terms the solubility product constant applies to the equilibrium between a precipitate and its ions, and therefore to a saturated solution of the former, as for example, $AgCl \rightleftharpoons Ag^+ + Cl^-$, $K = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$ and since the active mass or activity of silver chloride under these conditions is a constant, $[Ag^+]\,[Cl^-] = S_{AgCl}$, S denoting the solubility product constant, which applies at the temperature of the measurements. In as much as the activities of the ions are determined by the general electrical environment (total ionic strength), the principle is true in terms of activities rather than molecular concentrations. For the process: $BA \rightleftharpoons B^+ + A^-$, representing the activities of the ions by a_B, a_A, and the activity coefficients by f_B, f_A, $S_{BA} = a_B \times a_A = f_B[B^+]f_A[A^-]$ At extreme dilutions f_B and f_A become equal to unity, and the expression reduces to the simple classical form $S_{BA} = [B^+][A^-]$.

A classical example of the validity of the solubility product principle is given by the data in Table XVI.

TABLE XVI. EFFECT OF CHLORIDE ION UPON THE SOLUBILITY OF SILVER CHLORIDE[1]

Concentration of KCl	Concentration of Cl^-	Concentration of Ag^+	S_{AgCl}
0.00670	6.4×10^{-3}	1.7×10^{-8}	1.1×10^{-10}
0.00833	7.9×10^{-3}	1.39×10^{-8}	1.10×10^{-10}
0.01114	10.5×10^{-3}	1.07×10^{-8}	1.12×10^{-10}
0.01660	15.5×10^{-3}	0.738×10^{-8}	1.14×10^{-10}
0.03349	30.3×10^{-3}	0.388×10^{-8}	1.17×10^{-10}

With increasing concentration of foreign salt, the solubility and of course the solubility product increases slightly.

The effect of common and diverse ions upon the solubility of a somewhat more soluble substance, thallous chloride, is shown in Fig. 52 where the data of Bray and Winninghoff are represented graphically.[2]

Calculations Based upon Solubility Product Constants. These calculations reduce to simple algebraic ones, and in rough calculations are of the type $xy =$ const.; xy^2 or $x^2y =$ const., etc., where x or y is known. *Illustration.* Given the solubility product constant, $S_{AgCl} = 10^{-10}$, find the grams of AgCl dissolved in a saturated solution of the salt (a) In pure water; (b) In 0.001 N KCl; and (c) In 0.05 N $AgNO_3$ solution.

(a) In a saturated solution of AgCl in pure water:

$$[Ag^+] = [Cl^-] = \sqrt{1 \times 10^{-10}} = 10^{-5}\,M.$$

$$\text{Weight dissolved, gram} = 10^{-5} \times \text{Mol. wt. AgCl}$$

$$= 10^{-5} \times 143 = 0.00143 \text{ g. per liter.}$$

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[1] E.M.F. measurements of Jahn, Z. physik. Chem. **33**, 545 (1900) as given by Fales, Quantitative Analysis.

[2] Bray and Winninghoff, J. Am. Chem. Soc. **33**, 1663 (1911). For other interesting studies of the solubility product principle see: Noyes, Z. physik. Chem. **6**, 241 (1890); J. Am. Chem. Soc. **33**, 1807 (1911); Noyes and Bray, *ibid.* **30**, 1643 (1908); Harkins and Winninghoff, *ibid.* **33**, 1827 (1911); Harkins and Pearce, *ibid.* **38**, 3679 (1916); Harkins and Paine, *ibid.* **41**, 1155 (1919).

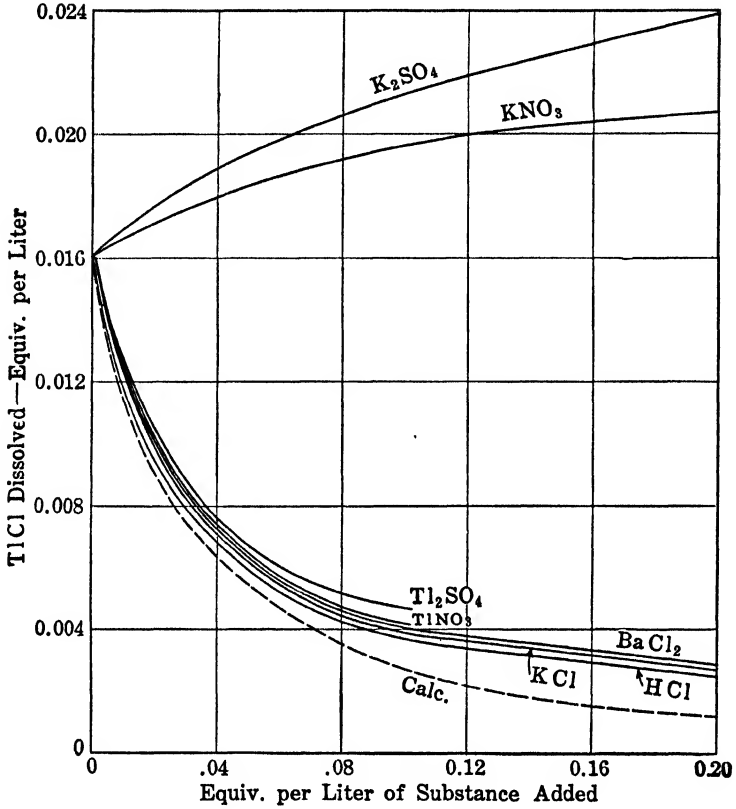

FIG. 52. Effects of Various Substances upon the Solubility of Thallous Chloride. The dotted curve is calculated for the effect of either thallium or chloride ion on the basis of activity set equal to concentration. The curves for K_2SO_4 and KNO_3 illustrate the diverse ion effect.

(b) Assuming that the chloride ion concentration is substantially that of the potassium chloride, i.e., 0.001 or 10^{-3} *M*,

$$[Ag^+] = \frac{10^{-10}}{[Cl^-]} = \frac{10^{-10}}{10^{-3}} = 10^{-7}\,M.$$

$$\text{Weight of silver chloride dissolved} = 10^{-7} \times 143$$

$$= 0.0000143 \text{ g. per liter.}$$

(c) Assuming $[Ag^+] = 0.05 = 5 \times 10^{-2}\,M$

$$[Cl^-] = \frac{10^{-10}}{5 \times 10^{-2}} = 2 \times 10^{-9}\,M$$

$$\text{Weight of silver chloride dissolved} = 2 \times 10^{-9} \times 143$$
$$= 0.00000029 \text{ g. per liter.}$$

A more refined calculation taking into account the change in concentration due to the slight amount of silver chloride that dissolves may be made. The solution of a simple quadratic equation is then called for. See Appendix.

The solubility product principle is more nearly rigorous· (a) The less soluble the precipitate, (b) the simpler the type of the precipitate, (c) the freer the solution from foreign ion. With precipitates of complicated types involving ions of high valence, e.g., $MgNH_4PO_4$; MoS_3; $K_2Zn_3(Fe(CN)_6)_2$, etc., the effects of hydrolysis, acidic properties (equilibria involving $HPO_4^=$, $H_2PO_4^-$, SH^-, etc.), and electrical interactions between ions of high valences, make it difficult to apply the principle in any simple fashion, although the effect of a slight excess of the reagent is in qualitative agreement with the principle in practically every case.

Effect of a Large Excess of Precipitant. There are many instances where an excess of a precipitant dissolves the precipitate first formed due to a further reaction involving definite compound formation, as for example, the solubility of silver cyanide in excess of potassium cyanide to form the soluble complex salt, $KAg(CN)_2$, or the solution of copper, nickel or cobalt hydroxide in ammonia to form complex salts, $Cu(NH_3)_4SO_4$, etc. In cases where no definite complex-formation is known to occur, a very large excess of the reagent frequently causes an increase in solubility. Many of these instances involve poorly defined or unstable complexes or a series of complexes. In some cases the nature of the solvent is modified.

(2) **Effects of Foreign Substances upon the Solubility of a Precipitate.** (a) **Effect of Salts.** *Diverse Ion Effect.* This effect is illustrated in Fig. 52, p. 292. The foreign ions modify the activity of the ions of the precipitate and the net effect is that they are less effective in recombining to form the precipitate

than when present at the same molar concentration in pure water. An increased solubility results. For this reason as well as for others discussed under "Purity of the Precipitate," p. 297 ff, an analytical precipitation is carried out at the maximum dilution that is consistent with substantially complete recovery of the substance to be determined.

The Formation of Complex Ions. If a slightly ionized complex or an undissociated salt is formed a precipitate that is virtually insoluble in water may be readily dissolved. The formation of complex ions, e.g., with ammonia, such as $Cu(NH_3)_4^{++}$, $Ag(NH_3)_2^{+}$, as well as those sulfosalts like $SnS_3^{=}$, etc., or cyanides, $Cu(CN)_3^{\equiv}$, is employed in qualitative analysis. Many quantitative procedures are based upon a knowledge of the relative tendencies of different substances to form stable complexes. A table of complex dissociation constants is given in the Appendix, (Table XXIII).

There appear to be gradations of solvent effect ranging from rather minor increase in solubility due to electrical interaction of ions, i.e., moderate diverse ion effect, up to complete solubility due to definite complex formation. These effects are avoided or utilized, as the situation demands, by suitable modifications of methods and procedures.

(b) *Effect of Acids and Bases upon the Solubility of a Precipitate.* The salt of a highly ionized acid is in general no more soluble in such acids than in salts. For example, the solubility of silver chloride is about the same in 0.001 *N* nitric acid as it is in 0.001 *N* potassium nitrate. If the precipitate is the salt of a slightly ionized acid, the solvent action may be very considerable, due to the withdrawal of anions of the precipitate:

$$\underset{\text{Precipitate}}{BA} \rightarrow B^+ + A^- + H^+ + Cl^- \rightarrow HA + B^+ + Cl^-$$

If the ionization constant of the acid is very small, the solution of the precipitate may proceed to completion. The following classes of substances that are almost insoluble in water dissolve readily in certain of the strong acids:

Arsenates of Ag and Pb.
Carbonates of Ca, Sr, Ba, Pb.
Chromates of Ag, Pb, Ba.

Oxalates of Ca, Ba, etc. Similar salts of many other organic acids.
Phosphates of Ag, Ba, etc.; also double ammonium phosphates of Mg, Mn, Cd and Zn.
Sulfates of Pb, and, to a lesser extent, Ba.

The dissolved portion of each of the salts in water exists as ions. The addition of an acid upsets the equilibrium between the precipitate and its ions by forming acids or ions with which the precipitate is not in a direct equilibrium, e.g., $H_2AsO_4^-$, $HAsO_4^=$, H_2CO_3 (decomposes), HCO_3^-, $HCrO_4^-$, $HC_2O_4^-$, $H_2PO_4^-$, $HPO_4^=$, HSO_4^-.

Illustrations:

$$\underset{\text{Ppt.}}{CaC_2O_4} \rightarrow Ca^{++} + C_2O_4^= + H^+ + Cl^- \rightarrow Ca^{++} + HC_2O_4^- + Cl^-$$

$$\underset{\text{Ppt.}}{Ag_3AsO_4} \rightarrow 3Ag^+ + AsO_4^{\equiv} + H^+ + NO_3^- \rightarrow 3Ag^+ + HAsO_4^= + NO_3^-$$

The effect is not very far reaching in the case of the sulfates because the ion HSO_4^- is very largely ionized, whereas ions like $HPO_4^=$ and $HAsO_4^=$ are extremely slightly ionized into hydrogen ions and the simple anions $PO_4^{\equiv}$, $AsO_4^{\equiv}$.

Bases. Most of the slightly ionized inorganic bases are so insoluble that analogous instances of solubility of salts of strong acids and weak bases in alkalies such as sodium or potassium hydroxide are difficult to find. When salts of this type that are insoluble in water are dissolved by strong alkalies the mechanism is usually through complex formation or through acidic properties. Example: Freshly precipitated stannic hydroxide (or acid) dissolved readily in an excess of potassium hydroxide;

$$SnCl_4 + 4KOH = Sn(OH)_4 + 4KCl.$$

$$\underset{\text{Pptd.}}{Sn(OH)_4} + 2KOH = \underset{\text{Soluble}}{K_2Sn(OH)_6}.$$

(3) Effect of Temperature upon the Solubility of a Precipitate. The majority of analytical precipitates are more soluble at higher than at lower temperatures. In many cases the solubility is so slightly increased when the temperature is raised from room temperature to 100° C. that the filtration may be made while the solution is hot. This is very advantageous because the impurities are in general more soluble and more readily washed away from the precipitate; due to decrease in viscosity hot solutions filter more rapidly, other factors being equal. Barium sulfate, the hydroxides of iron, chromium and aluminum and their basic acetates, etc., and many other substances are so slightly soluble that they may be filtered from hot solutions. On the other hand the double ammonium phosphates of magnesium, manganese or zinc, as well as lead sulfate and silver chloride should be filtered from cold solutions. The effect of temperature upon the solubilities of a few important analytical substances is shown in Table XVII.

TABLE XVII. EFFECT OF TEMPERATURE UPON SOLUBILITIES OF CERTAIN PRECIPITATES

Solubilities in Gram per 100 ml.

Temperature C.	Barium Sulfate	Silver Chloride	Calcium Oxalate	Magnesium Ammonium Phosphate	Lead Sulfate
15°	0.00021	....	....	0.0066	......
20°	0.00024	0.00015	0.00068*	0.0074	0.0041
100°	0.00031	0.0022	0.0014†	‡	0.0082

* At 25° C. † At 95° C. ‡ Decomposed by boiling with water.

At the beginning of a washing the solubility of a precipitate is materially diminished by the presence of an excess of one of its ions.

(4) **Effect of Nature of Solvent.** Certain precipitates are much less soluble in a mixture of water and a second solvent such as alcohol, dioxane, etc., than in water alone. The addition of 10 to 20 per cent of alcohol by volume makes the solubility of lead sulfate in the solution practically negligible.

Change of solvent. It is sometimes advantageous to evaporate the water from a solution after certain separations have been made. Two possibilities are then available. (a) Two substances in the residue may then be separated fairly effectively by treating the dry residue with a second solvent in which all but one of the substances is soluble. For example, an alcohol-ether mixture dissolves calcium nitrate and not strontium nitrate from a dried mixture of the two salts. (b) A second solvent may be of such nature that all of the substances dissolve, but upon adding a suitable reagent only the desired substance is precipitated. For example, potassium, rubidium and cesium are separated from sodium and lithium in a manner which leaves the sodium and lithium present as perchlorates in a *N*-butyl alcohol solution. Upon adding a solution of hydrogen chloride in *N*-butyl alcohol, the sodium is precipitated as sodium chloride and the lithium remains in solution.[1]

(5) **Effect of Time.** Certain precipitates tend to remain in supersaturated solution for long periods unless the solution is agitated or allowed to stand for several hours. Magnesium ammonium phosphate, the phosphomolybdates and the triple acetate precipitates often exhibit supersaturation phenomena to a pronounced degree. For all precipitates a certain period of "aging" in contact with the mother liquor is desirable in order that colloidal particles may be precipitated, and that the smaller particles may agglomerate and cement themselves together. This aging process involves the operation of many factors which tend to make the precipitate less soluble and more readily filterable. At elevated temperatures there is some evidence that the smaller particles of certain crystalline substances very slowly dissolve and recrystallize on the larger ones; this effect is unimportant at room temperature.

The Physical Character and the Purity of the Precipitate. The general conditions during an analytical precipitation have much to do with the filterability of the precipitate and its purity. The latter question is dealt with further in the Chapter on Separations, p. 371 ff. The physical character of the precipitate depends largely upon whether the initial or primary particles are crystalline or amorphous, and if crystalline, whether conditions are such that pronounced supersaturation occurs with resultant formation of a very large number of fine crystals as contrasted with slower growth from a relatively small number of centers of crystallization to form larger particles. Control of temperature and the rate of addition of the reagent determine in many cases whether the precipitate is filterable without loss as con-

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[1] Standard Methods of Chemical Analysis, 5th Ed., Vol. I, pp. 884–886, D. Van Nostrand Co. (from a chapter on the Alkali Metals by W. B. Hicks).

trasted with a very fine-grained or colloidal precipitate which readily passes through fine-textured filter paper or other filtering media.

Gelatinous precipitates. The hydroxides, or hydrous oxides, and the basic acetates, benzoates, formates, etc., of ferric iron, aluminum, chromium, etc., when formed by neutralizing the solution in the conventional manner, tend to precipitate in the amorphous condition in a gelatinous form that is intermediate between a colloidal sol and a colloidal emulsion. In the process of coagulation the particles, originally held apart by an adsorbed layer of hydroxide ions, adsorb positive ions which would be expected to remain in the filtrate, e.g., Cu^{++}, Ni^{++}, Zn^{++}, Ca^{++}, Mg^{++}, and these ions are difficult or impossible to wash out of the precipitate. The anions tend to take part in the formation of the charged colloidal particles, and are carried down during the precipitation.[1] The presence of a high concentration of ammonium ions tends to diminish the adsorption of other positive ions. The contamination of the precipitate is frequently so serious that the first precipitate must be filtered and washed, then dissolved, and the precipitate formed again in the solution now relatively dilute with respect to foreign ions.

The basic acetate procedure, and other analogous ones, have the advantage that the final stages of the neutralization are effected by slowly heating the solution and thus increasing the concentration of hydroxyl ions by increased hydrolysis and by the buffering effect of the acetate ions which combine with the hydrogen ions. A still greater improvement in the density and filtering qualities of the precipitate and therefore in the sharpness of the separations is effected by liberating ammonia slowly and uniformly throughout the boiling solution by the hydrolysis of urea added to the solution for that purpose: $CO(NH_2)_2 + H_2O \rightarrow \uparrow CO_2 + 2NH_3$. See pp. 349, 350 for a further discussion of the urea method, which was devised by Willard and Tang.[2]

Curdy Precipitates. The silver halides, silver molybdate, and other substances tend to separate in a curdy form, although their particles are shown by X-ray examination to be crystalline.

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[1] See Fig. 43, p. 170, Chapter IX and Fig. 54, p. 373. Chapter XVII and the accompanying discussion.

[2] H. H. Willard and N. K. Tang, J. Am. Chem. Soc. **59**, 1190 (1937); Ind. Eng. Chem. Anal. Ed. **9**, 357 (1937).

Kolthoff[1] explains this characteristic of these precipitates as being due to the fact that the primary particles have about the same solubility as the larger crystals, and hence there are many centers or nuclei of precipitation and there is little tendency for larger particles to grow at the expense of the smaller ones. The solution is very rapidly exhausted of ions that might tend to enlarge the particles, and the precipitate forms as a flocculated colloid. The flocculation is caused by the adsorption of ions of charge opposite to that of the sol particles. This adsorption is a surface phenomenon, and the precipitate tends to free itself of adsorbed ions upon aging. If a halide is being precipitated with silver nitrate, the presence of hydrogen ions is beneficial since the colloidal particles will then tend to be discharged by adsorption of hydrogen ions rather than silver ions.

Well-developed Crystals. If a precipitate is caused to form under conditions in which it is somewhat soluble, or if the primary particles have a solubility that is very much greater than the larger crystals, then the general tendency is for crystallization to start from fewer nuclei or centers of crystallization, and larger crystals tend to grow. This effect is not to be confused with the fact that a precipitate that was initially non-filterable due to too rapid precipitation may become filterable after digestion for some minutes or hours. After the particles have formed, the effect which may later aid filtration appears to be a cementing together of smaller particles, rather than a solution and reprecipitation of small particles on the larger ones.

Since the precipitates that are useful in analysis have low solubilities, there is always the possibility of producing a high degree of supersaturation by adding the reagent too rapidly. The crystallization then proceeds from a large number of centers. It is probably possible by extreme variation of concentrations and modes of addition to make any given precipitate form in either a gelatinous, curdy or visibly crystalline condition.[2] Under analytical conditions precipitates such as calcium oxalate and barium sulfate, for example, tend to precipitate in micro-crystalline or even curdy form that is difficult or impossible to filter

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[1] I. M. Kolthoff, J. Phys. Chem. **36**, 860 (1932).

[2] Von Weimarn demonstrated the fact that barium sulfate could be prepared as a gelatinous mass by rapid mixing of concentrated solutions, or in curdy form by rapid mixing of less concentrated solutions.

if the reagent is added too rapidly, whereas with slow addition of reagent and with the solution at elevated temperature, crystals that are readily filtered are obtained. The ideal process is one involving an internal reaction which forms in the solution itself the substance needed for precipitation without the addition of the reagent. This condition cannot often be realized but an example of it has already been mentioned in the use of urea to form ammonia in the precipitation of hydroxides (p. 298).

In any precipitation in which the reagent is dropped in slowly from a buret or a pipet, there is more or less locally increased concentration and opportunity for foreign substances to build into the crystals as they form. If the precipitate is a flocculated sol, the adsorption is superficial. With crystals that grow to appreciable size there is adsorption during the growth of the crystals, and this process is distinguished by Kolthoff (loc. cit.) as the real co-precipitation process. These impurities are to be regarded as imperfections in the lattice of the crystal. During the process of digestion at an elevated temperature the imperfect crystals which are rather loosely joined mosaics of crystalline blocks tend to undergo a certain amount of recrystallization and rearrangement which tends to perfect the structure somewhat and to force out the impurities; the net effect of this accelerated aging process is to give a purer and more readily filterable precipitate.

SUMMARY OF RULES FOR ANALYTICAL PRECIPITATIONS

1. The reagent and the solution containing the ion that is to be precipitated should be as dilute as is compatible with the solubility of the substance, and with the number of subsequent operations that are to be made upon the filtrate. 2. If the use of heat is permissible one or both of the solutions is kept just below boiling during the precipitation. 3. The reagent is added slowly and with stirring until a slight excess of the precipitating ion is present. In exceptional cases a rather large excess of the reagent may be needed, usually to perform a second function such as buffering the solution. 4. A certain period of time must be allowed for completion of the precipitation. Digestion at a temperature of 90-95° C. improves the filterability and the purity of many of the analytical precipitates.

If a prohibitive amount of contamination of the precipitate occurs in spite of the observance of these rules, either a separation of interfering ions must be made before the precipitation is attempted, or the precipitate may be filtered, washed, dissolved and reprecipitated.

The Washing of Precipitates. The details of filtration have been considered in Chapter II, p. 24 ff. After the precipitate has been formed and aged, the supernatant liquid is decanted through the filter, after which it is frequently advantageous to treat the precipitate with a rather large number of small portions of wash solution in the vessel in which the precipitation was made, stirring each portion of wash liquid into thorough contact with the precipitate, allowing the latter to settle, decanting most of the liquid through the filter, etc. Washing in this manner is fairly effective for gelatinous precipitates, whereas washing them after transfer to the filter is usually an imperfect and inefficient process. The principle of distribution is followed in using small portions of wash liquid. If used in four or five portions, a given volume of liquid is many times as effective as when used in one or two portions. Portions of the filtrate are tested qualitatively from time to time in order to be convinced that the foreign substances have been removed. If further precipitations are to be made of substances in the filtrate, tests must be devised that will add no undesirable substances.

The Choice of a Wash Liquid. Comparatively few precipitates can be washed with water. After a certain period of washing the ions which caused the neutralization of the charge of the colloidal particles may diffuse out and the particles will then tend to return to the colloidal state of subdivision and pass through the filter. The choice of a suitable wash solution is therefore an important matter. The choice is governed by the following questions: 1. Will water dissolve an appreciable amount of the precipitate? 2. Will the precipitate tend to become gelatinous or colloidal? If so the filter may become clogged, or the precipitate may run through. 3. Will water wash out completely the substances to be removed? 4. Will the wash solution be entirely without action on the precipitate, and if the precipitate is to be weighed will the wash liquid remaining in contact with it leave any weighable residue after drying or ignition?

All wash solutions may be divided into three classes:

Solutions which reduce the solubility of the precipitate. This may be effected in two ways: (a) By adding a moderate concentration of a substance with one ion in common with the precipitate. Use is made of the general tendency of substances to be less soluble in the presence of a slight excess of a common ion. (b) By the use of some organic solvent such as alcohol, ether, etc. Most salts are insoluble in alcohol and similar solvents, and even in a mixture of alcohol and water the solubility is often reduced to a negligible quantity. Occasionally method (a) or (b) alone is insufficient, and the solubility of certain precipitates may be still further reduced by combining these methods. Illustrations are the washing of strontium sulfate or of lead sulfate with a mixture of diluted sulfuric acid and alcohol. Comparatively few substances are so insoluble that 100 ml. of water will not dissolve an appreciable amount of material. Among the very insoluble precipitates are the hydrous oxides of the weak bases such as ferric iron, aluminum, chromium, tin, etc.; the sulfides; barium sulfate; the silver halides; lead chromate. The effectiveness of this first type of wash solution is illustrated by the fact that 100 ml. of water at 25° C. dissolves 0.7 mg. of calcium oxalate, while the same volume of dilute ammonium oxalate has practically no solvent action on this salt. On the other hand, calcium oxalate is dissolved by dilute ammonium hydroxide, which has no ion in common with it, to about the same extent as by water. One hundred ml. of water dissolves 4.1 mg. of lead sulfate, but dilute sulfuric acid or 50 per cent alcohol exerts practically no solvent action on this substance.

Solutions which prevent the precipitate from becoming colloidal and running through the filter. This tendency is rarely shown by precipitates that are in a well-defined crystalline condition, but is very frequently observed with those of the gelatinous or flocculated colloid type, which are aggregates of very fine particles, sometimes held together by rather feeble forces. Wash solutions of this second class contain an electrolyte, which may be an acid, base or a salt,—most frequently the last. The nature of the electrolyte is immaterial as long as it is without action upon the precipitate either during washing or ignition. Ammonium salts are, therefore, largely used.

Among the precipitates of gelatinous or flocculated character are the oxides, the hydroxides, the sulfides and the silver halides.

For example, hydrous ferric oxide or hydroxide is washed with ammonium nitrate solution. Ammonium chloride is equally efficient for washing, but would cause the formation of volatile ferric chloride during the ignition of the precipitate. Sodium or potassium salts are unsuitable because they are not volatilized on ignition. Silver chloride is washed with one per cent nitric acid which is without action on the precipitate and is easily volatilized. Hydroxides are, of course, dissolved by acidic wash solutions. It is sometimes necessary to use a wash solution which serves the double purpose of reducing the solubility of the precipitate and preventing it from becoming colloidal.

Solutions which prevent the hydrolysis of salts of weak bases or acids. If salts of weak bases such as ferric iron, aluminum, chromium, tin, etc., are being separated from a precipitate, e.g., silica, by washing with water, the salts tend to hydrolyze and their insoluble basic salts or hydroxides are retained by the filter paper:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl.$$

Since an acid is formed in hydrolyses of this type, the addition of an acid to the wash solution will prevent any hydrolysis of ferric salts or others of this type. Dilute hydrochloric acid is used as a wash solution to remove ferric and aluminum salts from precipitates that are insoluble in this acid.

If the precipitate itself is sufficiently soluble it may, if a salt of a weak acid or a weak base, show a tendency to hydrolyze. Since the precipitate is usually the salt of a weak acid, the soluble product of hydrolysis in this case will not be an acid, but a base; therefore the wash solution must be alkaline. Such cases are rare. An example is magnesium ammonium phosphate, $MgNH_4PO_4$, which hydrolyzes to give magnesium acid phosphate, $MgHPO_4$, and ammonium hydroxide, and which should, therefore, be washed with dilute ammonium hydroxide. Manganese ammonium phosphate, however, may be washed with water since it is so much less soluble that hydrolysis is inappreciable. It should be remembered that only the salts of weak or highly insoluble bases or acids can hydrolyze.

Summary. The following points should always be considered when choosing a wash solution: First, the solubility of the precipitate; Second, its nature—whether crystalline, flocculated colloid or of gelatinous character; Third, what substances are to be washed out—whether they are soluble in pure water without hydrolysis, and also whether the precipitate if slightly soluble, may be appreciably hydrolyzed. In addition one must be certain that the wash solution chosen is without action on the precipitate under all conditions to which it will be exposed, and that any electrolyte in the wash liquid is completely volatile at the temperature to which the precipitate is heated, unless the latter is not to be weighed.

THE DRYING AND IGNITION OF PRECIPITATES

The marking of crucibles for identification and the manner of heating a porcelain crucible, or a Gooch crucible has been considered in Chapter II. (See Fig. 15, p. 32 and Fig. 16, p. 33.)

Drying. Certain precipitates and electrolytic deposits will lose water, volatilize or become oxidized, etc., at temperatures below 100° C. Such substances are collected, when possible in filtering crucibles, and washed finally with alcohol followed by ether, or by other suitable volatile solvents. The volatile solvent is then removed by allowing the crucible to stand in a desiccator for a sufficient time. Frequently a desiccator provided with a side arm and stop-cock is used, and the desiccator is partially evacuated with a filter pump, in order to speed the removal of the ether or other solvent. Metallic mercury, certain hydrates, and certain metallic salts of organic precipitants must be dried either at room temperature or at some definite moderate temperature, e.g., 60° C., 80° C.

Ignition. Precipitates that are easily reducible by paper are collected, when possible, upon filter crucibles of glass, porcelain or platinum. After drying at 100° C. or by heating gently within a protecting crucible (Fig. 16, p. 33) the temperature is brought to the final suitable range, if this is much higher than 100° C., with the aid of a burner, or preferably in an electric oven or muffle furnace.

If a reducible precipitate must be filtered on paper, for example, because no filtering crucible will stand the heating to the high temperature and subsequent cooling, then it may be necessary to dry the paper filter[1] and remove the major part of the precipitate carefully to a clean watch glass over a glazed paper. The precipitate is covered with a beaker or other glass vessel while the paper is being burned carefully in a weighed porcelain crucible. If particles of the precipitate are converted to metal in this process they are brought back to the desired form by treatment with appropriate acid, ammonium salt or other volatile reagent before the major portion of the precipitate is transferred to the crucible. A small brush with fibers of ashless material is used in completing the transfer. This type of manipulation which was once the rule rather than the exception is now avoided in all possible cases through the use of filtering crucibles, or by the development of new reagents and new methods.

If the precipitate is not readily reduced by paper and its decomposition products that are formed by gentle heating, the moist precipitate and its contents are transferred to a suitable weighed crucible. If precipitate adheres to the funnel it may be wiped out with a small piece of ashless paper which is added to the precipitate. If the crucible is of platinum it is gently heated on a triangle of platinum or nichrome in an inclined position with the heat applied mainly at a point about one third of the way down from the mouth. Heat is conducted down to the paper and in the later stages of the decomposition the contact with platinum greatly aids the low temperature removal of the paper. In a porcelain crucible the process is slower, and many prefer to start the heating with the crucible upright on a nichrome or other suitable triangle and the top about ⅛ inch open at one point to avoid the sticking of the lid due to the distillation of tarry material from the paper. At no time should the paper or its gaseous decomposition break into flame. After the paper has been thoroughly charred the crucible is inclined toward an apex of the triangle and the lid tilted against the mouth to circulate air toward the precipitate (Fig. 15, p. 32). From time to time the crucible is rotated around its vertical axis and the flame is

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[1] The funnel is covered with a piece of filter paper previously marked with the proper identifying symbols and moistened with distilled water.

gradually increased until all of the carbon has burned away. Finally the crucible is heated for 10-15 minutes at the proper temperature with the aid of a Bunsen burner, a Meker or blast flame, or an electric furnace. If a blast lamp is to be used the flame is adjusted, and after the crucible has been warmed the oxidizing part of the flame is allowed to play against the lower part of the crucible; the axis of the blast flame is adjusted at an angle of about 45° with the table top, and the crucible is slanted out and up so that its vertical axis makes approximately a right angle with that of the flame.

After partial cooling in the air the crucible is cooled for 30-40 minutes in a desiccator, then with its contents it is weighed, then reheated, cooled and weighed until the weight is constant to within 0.0002 g.

In a few cases it is desirable to treat the cold precipitate chemically between weighings in order to be sure that any slight action of the paper during the ignition has been remedied. Sulfates of lead, barium, etc., may be moistened with a small drop (0.02-0.03 ml.) of dilute sulfuric acid. The excess of acid is expelled by cautious heating by moving a tiny flame slowly back and forth well below the bottom of the crucible as it rests upright on a triangle with the cover slightly ajar. By this action BaS, if present, is converted back to $BaSO_4$, etc. A small lump of ammonium carbonate is often added to a stannic oxide precipitate to aid in the removal of adsorbed anions, e.g., sulfate. Ammonium nitrate or fuming nitric acid is sometimes added in order to oxidize particles of carbon from the filter paper; a better alternative is to lead in purified oxygen gas cautiously through a flanged porcelain tube that fits through a hole in a special cover (Rose's crucible cover). These special manipulations are of use in occasional determinations after some skill has been acquired, but are troublesome and time-consuming; the modern tendency is to develop procedures in which they are unnecessary.

THE CALCULATIONS OF GRAVIMETRIC ANALYSIS

(1) After separating and weighing the element which is to be determined in a substance, the percentage of it may be calculated by a proportion.

If W is the weight of sample used in the analysis, and w the weight of the element found, then

$$W : w = 100 : x,$$

where x is the percentage of the element sought.

(2) The percentage of an element in a certain substance may be found by precipitating the element in the form of one of its stable compounds, and weighing the latter.

If W is the weight of the sample, and w the weight of the precipitate (in this case a pure compound), the weight of the element in the compound may be calculated in the following way:

Mol. wt. of compound : No. of gram at. wts. of element per mol. wt. of compound $= w : y$, where y is the weight of the element sought.

Then $W : y = 100 : x$, where x is the percentage sought.

Illustration: A 1.0020 g. sample of an iron salt was dissolved, and after suitable treatment, all of the iron was precipitated as hydrous ferric oxide, and converted finally into ferric oxide, Fe_2O_3, which weighed 0.1663 g. Find the percentage of iron in the salt.

$$\underset{(\text{Mol.Wt. } Fe_2O_3)}{159.70} \quad : \quad \underset{(2 \times \text{At.Wt. Fe})}{111.70} \quad = 0.1663 : y.$$

$$y = \frac{111.70}{159.70} \times 0.1663 = 0.1163 \text{ g. of iron.}$$

Then $1.002 : 0.1163 = 100 : x.$

$$x = 11.61 \text{ per cent of iron.}$$

Note that there is a constant ratio occurring in the determination of any one substance; in this case the ratio is

$$\frac{111.70}{159.70} = 0.6994.$$

The following discussion will illustrate further the method of calculation in a somewhat more complicated case.

It is not always the percentage of an element in the substance analyzed that is desired. From the weight of pure precipitate found, it is possible to calculate the amount of any substance which is equivalent to it.

Illustration. The sulfur in a substance has been converted into a soluble sulfate, and then precipitated in the form of barium sulfate. It is desired to find how much sulfur trioxide, SO_3, is equivalent to the sulfur present in the sample. From the reasoning already given, the following equality of the ratios is derived:

Mol. wt. SO_3 : Mol. wt. $BaSO_4$ $= x$: wt. of precipitate, since there is one molecule of sulfur trioxide in one molecule of barium sulfate. These ratios may be conveniently expressed as fractions, a method which is often preferred. Then,

$$\underset{(\text{wt. of SO}_3)}{x} = \text{wt. of BaSO}_4 \times \frac{\text{mol. wt. SO}_3}{\text{mol. wt. BaSO}_4}.$$

It is evident that part of this expression is a constant, viz.,

$$\frac{\text{mol. wt. SO}_3}{\text{mol. wt. BaSO}_4},$$

and may be calculated once for all by substituting the proper numbers, thus:

$$\frac{80.06}{233.46} = 0.3430;$$

this number may be used in all calculations involving the conversion of $BaSO_4$ into SO_3. Thus:

$$\text{wt. of SO}_3 = (\text{wt. of BaSO}_4) \times 0.3430.$$

This number is called the factor for converting $BaSO_4$ into SO_3. It is evidently the amount of SO_3 per unit weight of $BaSO_4$. Tables of these factors will be found in a number of handbooks of constants. Having obtained the weight of SO_3 in the precipitate and hence in the sample, the percentage is obtained simply by dividing this weight by the weight of the sample and multiplying the quotient by 100. Thus:

$$\frac{\text{wt. of SO}_3\text{ in sample}}{\text{wt. of sample}} \times 100 = \text{per cent of sulfur trioxide in the sample.}$$

It is advisable to use logarithms or a slide rule for the calculation of results, since either method saves time and greatly lessens the chance of making a numerical error. The logarithm of the conversion factor 0.34297 is -1.53526. Five place logarithms are sufficient. Only four significant figures should be retained in the percentages of substances reported.

The above case is the simplest one possible. A more complicated one will be considered—the calculation of the amount of SO_3 in a sulfate containing more than one atom of S, as $Al_2(SO_4)_3$. Then,

$$\frac{\text{wt. } SO_3}{\text{wt. } Al_2(SO_4)_3} = \frac{3 \times \text{mol. wt. } SO_3}{\text{mol. wt. } Al_2(SO_4)_3},$$

which

$$\text{wt. } SO_3 = \text{wt. } Al_2(SO_4)_3 \times \frac{3 \times \text{mol. wt. } SO_3}{\text{mol. wt. } Al_2(SO_4)_3}.$$

In this case the conversion factor would be $\frac{3SO_3}{Al_2(SO_4)_3}$.

The following is another illustration of these principles. The iron in a sample of Fe_3O_4 is converted into Fe_2O_3, which is weighed. To calculate the weight of Fe_3O_4:

$$\frac{\text{wt. } Fe_3O_4}{\text{wt. } Fe_2O_3} = \frac{2 \times \text{mol. wt. } Fe_3O_4}{3 \times \text{mol. wt. } Fe_2O_3},$$

and the conversion factor would be $\frac{2Fe_3O_4}{3Fe_2O_3}$, in order to obtain equality in the number of atoms of iron. If the weight of ferrous oxide was desired, the factor would be $\frac{2FeO}{Fe_2O_3}$, and so on for all possible compounds.

The important points to be remembered are these, and failure to remember them is the cause of most of the errors made by the student in calculating the results of gravimetric analyses:

1. *The number of molecules of each of the two substances in a gravimetric ratio must be such that they contain the same number of atoms of the particular element involved.*

2. *When the ratio is expressed as a fraction to be used as a gravimetric conversion factor, the molecular weight of the substance weighed or a proper multiple of this is always placed in*

the denominator and that of the substance sought in the numerator.

3. *In forming the ratio only the substance weighed and the substance sought are considered. All intermediate products are disregarded.* This last point can always be observed by writing balanced equations for the successive reactions, and finding thus the number of molecules of substances weighed and sought, even though these substances may have no elements in common. Thus, arsenic is converted into silver arsenate and the latter into silver chloride, which is weighed:

$$As \rightarrow Ag_3AsO_4 \rightarrow 3AgCl.$$

Therefore the conversion factor to be used in calculating the weight of arsenic equivalent to a definite weight of silver chloride is $\frac{As}{3AgCl}$.

In each of the following cases, indicate the ratio of the molecular weights for the conversion factor, but do not calculate the factor:

Substance Weighed	Substance Sought	Conversion Factor
$BiPO_4$	Bi_2S_3	
Mn_3O_4	Mn_2O_3	
$Mn_2P_2O_7$	Mn_3O_4	
$AgCl$	$Ag_4Fe(CN)_6$	
Al_2O_3	Al_4C_3	
$BaSiF_6$	CaF_2	
$BaSO_4$	K_3AsS_4	
AgI	$KIO_3.HIO_3$	
$KClO_4$	$AlF_3.3KF$	

A loss or gain in weight due to some definite chemical reaction may be used in a calculation just as if it were a chemical substance. Bromide ion is often determined in the presence of chloride ion by precipitating both ions in the form of their silver salts (AgCl and AgBr), and heating the mixture in an atmosphere of chlorine:

$$2AgBr + Cl_2 = 2AgCl + Br_2.$$

The loss in weight resulting from the displacement of bromine by chlorine is

$$\mathrm{AgBr} - \mathrm{AgCl} = \mathrm{Br} - \mathrm{Cl} = 79.92 - 35.46 = 44.46.$$

In finding the conversion factor, Br is the substance sought and Br − Cl the substance weighed:

$$\frac{\mathrm{Br}}{\mathrm{Br} - \mathrm{Cl}} = \frac{79.92}{44.46} = 1.7976.$$

In making calculations the rule is followed that only one uncertain figure shall be retained in the final result. For example, if the weight of sample used contains four significant figures (as 0.1544 gram), and if the accuracy in weighing is not greater than ± 0.1 − 0.2 mg., the value of the last number in the weight is uncertain. Therefore the final result of such an analysis should be expressed in four significant figures.

Factor-Weight Samples. For any particular type of determination, a weight of sample may be calculated such that the percentage of the substance sought may be found from the weight of precipitate without any computation except that of pointing off. The calculation of the percentage involves the following steps:

$$\text{wt. of ppt.} \times \text{conversion factor} = \text{wt. of subst. sought},$$

and

$$\text{wt. of sample} : \text{wt. of subst. sought} = 100 : x \text{ (per cent)}.$$

Hence

$$x = \frac{\text{wt. of ppt.} \times \text{conversion factor} \times 100}{\text{wt. of sample}}$$

This general formula may be used to solve any problem of the types discussed, in which there is adequate information about three of the four quantities.

Illustration. It is desired to take such a weight of a sample of a sulfate that each 0.01 g. of barium sulfate found shall indicate 1 per cent of sulfur in the original material. The factor in question is $\frac{\mathrm{S}}{\mathrm{BaSO_4}} = 0.1374$.

Then

$$1 = \frac{0.01 \times 0.1374 \times 100}{\text{wt. of sample}}, \text{ or wt. of sample} = 0.1374 \text{ g.}$$

Hence if 0.8295 g. of barium sulfate was found in a given case, the original material contained 82.95 per cent of sulfur. That is, this problem has been solved by taking a weight of sample that is numerically equal to the factor; problems of this general type are therefore known as factor-weight problems.

Indirect Analysis. It is theoretically possible to derive the percentages of two pure substances in a mixture without an actual separation. This type of process is avoided, wherever possible, because most of the experimental error usually falls upon one of the quantities derived by calculation, or because a small variation in some determinable quantity corresponds to too large a variation in percentage.[1]

Two substances which have one common constituent, as for example potassium chloride and sodium chloride, may be weighed together; the amount of the common constituent, in this case chlorine, is then determined. Or the original substances may be converted into a second pair of substances with a second common radical. For example, a mixture of NaCl and KCl may be converted into a mixture of Na_2SO_4 and K_2SO_4 and the mixture reweighed. The following illustration given by Caley (loc. cit.) will serve to demonstrate a simple method of attack on the first type of problem.

A mixture of potassium and sodium chloride weighed 0.2230 g. The chlorine in the mixture was determined gravimetrically and weighed 0.1285 g. The percentage of NaCl and KCl in the mixture is to be found.

If the 0.2230 g. of material consisted entirely of NaCl, the weight of the chlorine in it would be:

$$0.2230 \times \frac{35.46}{58.46} = 0.1353 \text{ g.}$$

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[1] The calculations of indirect analyses are described in some of the texts and books on calculations listed in the Appendix. Caley, J. Chem. Education 6, 1979 (1929) has presented the principles of such calculations in a concise manner.

Similarly, if it had been pure KCl, the weight of chlorine would be:

$$0.2230 \times \frac{35.46}{74.56} = 0.1061 \text{ g.}$$

Having thus found the limits and hence the range of possible weights of chlorine, the percentages of the two chlorides in the mixture may be calculated by proportion:

$$(0.1353 - 0.1285) : 0.1353 - 0.1061) = x : 100.$$
$$x = 23.28 \text{ per cent of potassium chloride.}$$

The above proportion might be set down in words as

Interval (no KCl to actual per cent KCl) : interval (no KCl to 100 per cent KCl) = per cent KCl : 100 per cent.
The per cent of NaCl = 100 − 23.28 = 76.72.

The latter percentage could be calculated by proportion:

$$(0.1285 - 0.1061 : (0.1353 - 0.1061) = y : 100,$$

where y denotes the per cent of sodium chloride.

If the experiment had consisted in treating the mixture of sodium and potassium chlorides with excess of sulfuric acid, heating to expel the hydrogen chloride and the unused sulfuric acid, and weighing the mixture of sodium and potassium sulfates, the problem could be solved along similar lines, by finding first the possible range from pure sodium sulfate to pure potassium sulfate for the weight of material in question.

Problem. Given the information that 0.4550 g. of a mixture of sodium and potassium chlorides yielded 0.5415 g. of sodium and potassium sulfates when treated in the manner just described. Calculate the percentages of sodium and potassium chlorides in the mixture.

In addition to the method of solution that has been described, an algebraic method may be used, or a graphical method of solution may be employed. For the first problem,

Let

$$x = \text{wt. of potassium chloride;}$$

then

$$0.2230 - x = \text{wt. of sodium chloride},$$

and

$$x\frac{\text{Cl}}{\text{KCl}} + (0.2230 - x)\frac{\text{Cl}}{\text{NaCl}} = 0.1285.$$

By replacing the symbols by the corresponding atomic weights, the value of x is readily calculated. The defects of indirect analyses are so serious that further discussion of these methods of calculation seems unnecessary in a book of this scope.

Review Questions and Problems

1. Formulate solubility product expressions for each of the following substances: Silver molybdate; magnesium hydroxide; silver ferricyanide; arsenic trisulfide; calcium carbonate.

2. List one or more wash solutions that would probably serve for each of the precipitates mentioned in 1.

3. $S_{AgCl} = 10^{-10}$, how much dissolved silver is there in 500 ml. of a solution that is 0.001 *M* in chloride ion and in equilibrium with solid silver chloride?

4. A 200 ml. portion of solution is 0.01 *N* in oxalate ion and saturated with calcium oxalate. How much anhydrous calcium oxalate is dissolved in the solution if the solubility product of calcium oxalate is 2×10^{-9}? Ans. 0.00001 g.

5. The solubility product of silver chromate is 2×10^{-12}. How much silver chromate in grams is present (*a*) in 5.00 liters of the saturated solution in pure water? (*b*) in 500 ml. of a solution that is 0.001 *N* in silver ion?

Ans. (*a*) 0.1317; (*b*) 0.00033 g.

6. The solubility products of silver chloride and silver cyanide are 10^{-10} and 2×10^{-12} respectively. Which is the better form in which to precipitate silver? Reasons?

7. The solubility of silver chloride is 0.0022 g. per 100 ml. at 100° C. Calculate the solubility product at this temperature.

8. The solubility product of magnesium hydroxide is 1.2×10^{-11}. (*a*) At what *p*H should the hydroxide begin to precipitate in a solution that is 0.005 *M* in magnesium chloride? (Assume the magnesium chloride to be completely ionized.) (*b*) If a solution were 0.005 *M* in magnesium chloride and 0.001 molar in ammonium hydroxide ($K_b = 10^{-4.76}$), would a precipitate of magnesium hydroxide be expected to form?

Ans. (*a*) *p*H 9.7; (*b*) Yes, because the *p*H is estimated to be 10.12.

9. Repeat the calculation in part (*b*) problem 8, for a solution that is 0.01 *M* in magnesium chloride (assumed to be completely ionized), 0.01 *M* in ammonium hydroxide, and 0.1 *M* in ammonium chloride (assumed completely ionized).

10. For barium sulfate, $S_{BaSO_4} = 10^{-10}$, calculate (*a*) the amount soluble, in moles, and (*b*) the amount soluble, in grams, in 2.00 liters of a solution that contains 0.0077 g. of ammonium sulfate per 100 ml. (The ammonium sulfate assumed to be completed ionized.)

11. The solubility product of ferrous hydroxide is 2×10^{-14}. Calculate whether the hydroxide would precipitate in a solution 0.01 *M* in ferrous ion, 0.1 *M* in ammonium ion and 0.01 *M* in ammonium hydroxide.

12. A 0.4825 g. sample of an alloy of copper and silver was dissolved in nitric acid and the silver recovered quantitatively as silver chloride which weighed 0.5768 g. Calculate the per cent of silver in the alloy.

13. A mixture is known to contain not more than 10 per cent of potassium bromide, the remainder being potassium nitrate. How much 0.5 *N* silver nitrate should be used to precipitate the bromide in a 0.4000 g. sample of the substance?

14. The arsenic in a 0.4964 g. sample of an arsenate was converted quantitatively into arsenic pentasulfide and the weight of the latter was found to be 0.3320 g. Calculate (*a*) the per cent of arsenic, and (*b*) per cent of arsenic pentoxide in the arsenate.

Ans. (*a*) 32.31 per cent; (*b*) 49.56 per cent.

15. How much of an aluminum salt would you weigh out in order that each 0.02000 g. of aluminum oxide found should represent 1 per cent of aluminum in the material?

16. Calculate the following gravimetric factors: Desired lead monoxide, weighed lead sulfate; Desired potassium bichromate, weighed chromic oxide; Desired manganese, weighed manganese pyrophosphate.

17. A sample consisting of a mixture of sodium and potassium chlorides weighed 0.4520 g. All of the chloride was converted into silver chloride which weighed 0.9785 g. Calculate the per cent of sodium and per cent of potassium in the mixture.

18. A 0.3684 g. sample of iron pyrites yielded 0.1910 g. of ferric oxide. Calculate the percentage of FeS_2 in the mineral on the assumption that this was the only iron compound present in it.

19. A sample weighing 0.5000 g. of a substance containing magnesium yielded on proper analysis 0.2830 g. of pure magnesium pyrophosphate. Calculate the per cent of magnesium oxide in the material.

20. A mixture contained calcium hypochlorite, lime and moisture. A sample of the mixture weighing 0.5000 g. was so treated that all of the chlorine present in it was converted into silver chloride that weighed 0.8375 g. Calculate the per cent of calcium hypochlorite ($CaOCl_2$) in the mixture.

21. A 1.0000 g. sample of a substance yielded 0.3640 g. of ferric and aluminum oxides. The mixture of oxides when heated in hydrogen lost 0.0786 g. Calculate the percentages of iron and of aluminum in the original material.

22. A 0.6200 g. sample of a mixture of magnetite (Fe_3O_4) and insoluble siliceous material was treated with acid and the total iron recovered as ferric oxide, weighing 0.3500 g. Find the per cent of magnetite in the material.

23. The ignited precipitate of lime (CaO) from a 1.0000 g. sample of a mineral was treated with ammonium carbonate and converted into calcium carbonate. The gain in weight was 0.0927 g. Calculate the per cent of calcium oxide in the mineral.

CHAPTER XVI

SIMPLE GRAVIMETRIC DETERMINATIONS

The order in which determinations should be carried out by the student depends somewhat upon the objectives of the course. The material in this chapter has been arranged in what is believed to be the order of increasing difficulty or complexity. Each procedure is complete in itself, so that departures from this order should offer no difficulty to student or teacher.

DETERMINATION OF HALOGEN IN A HALIDE. CHLORINE IN A CHLORIDE

Principle. The chloride is dissolved in water, and the solution is acidified with nitric acid in order to obtain a better precipitate and to prevent the precipitation of other silver salts (such as the phosphate, the carbonate, etc.) which might form in a neutral solution. The chloride is precipitated as the silver salt by the addition of a slight excess of silver nitrate.

$$(1)\quad NaCl + AgNO_3 = \downarrow AgCl + NaNO_3.$$

To coagulate the precipitate into curds the solution is heated, and stirred or shaken vigorously. The precipitate is then filtered through a filtering crucible, washed with very dilute nitric acid to prevent it from becoming colloidal, dried at 150-200° C., and weighed as silver chloride. If a paper is used for the filtration, a procedure which is not advised, the filter is finally washed with water to remove acid which would attack the paper when dried. The paper is burned separately, and after converting the reduced silver back to silver chloride the main precipitate is added to the crucible and is dried at about 200° C. and weighed.

Errors. Silver chloride, if properly precipitated, shows comparatively little tendency to occlude other salts, and the spongy nature of the precipitate makes thorough washing possible. The solubility of silver chloride is only 0.14 mg. per 100 ml. of water at 20° C., but this value increases to 2.2 mg. at 100° C. The solubility of the salt is increased by the presence of ammonium and other alkali salts, and by large concentrations of acids, although very dilute nitric acid is without effect and very dilute hydrochloric acid decreases the solubility, owing to the presence of a common ion. Silver chloride is a flocculated colloid and therefore shows a tendency to become colloidal and run through the filter as the adsorbed ions are removed by washing. For this reason the wash solution used should contain an electrolyte. Nitric acid is chosen because it is without action on the precipitate and is readily volatile. If silver, instead of chloride ion, were being determined, dilute hydrochloric acid could be used as a wash solution and it would have the further advantage of decreasing the solubility.

Silver chloride is readily acted on by light, which decomposes it into silver and chlorine. The silver remains colloidally dispersed in the silver chloride and thereby imparts to it a purplish color. The decomposition by light is only superficial, and is negligible unless the precipitate is exposed to bright light and is stirred frequently. Therefore silver chloride should be protected from bright light as much as possible. The extent of this error may be illustrated by the following data from researches of Lundell and Hoffman: [1]

(a) In the solution containing silver chloride and excess of hydrochloric acid,

Wt. of AgCl Calculated	Wt. of AgCl Found	Error	Conditions of Exposure to Light
1. 1.3971	1.3915	−0.0056	2 hrs. in direct sunlight; no stirring
2. 1.3971	1.3948	−0.0023	7 hrs. in north light; occasional stirring
3. 0.7859	0.7851	−0.0008	2 hrs. in a bright laboratory; no direct or reflected sunlight; occasional stirring

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[1] Lundell and Hoffman, J. Research Natl. Bur. Standards **4**, 109 (1930).

(b) In a solution containing silver chloride and 1-2 per cent excess of 0.2 *N* silver nitrate,

	Wt. of AgCl Calculated	Wt. of AgCl Found	Error	Conditions of Exposure to Light
1.	1.2903	1.3179	+0.0276	5 hrs. in direct sunlight; occasional stirring
2.	0.5184	0.5194	+0.0010	2 hrs. in a bright laboratory; no direct or reflected sunlight; occasional stirring

When chloride ion is present in excess, the error is always negative due to the loss of chlorine which escapes from the precipitate. In such cases the weight of precipitate may be brought up to the correct value by treatment of the material with nitric acid followed by hydrochloric acid. In the reverse case (excess of silver ion) more silver is precipitated than that equivalent to the chlorine present, because the chlorine that is liberated by the action of light combines with silver ions in the solution and precipitates more silver chloride:

$$(2)\quad 3Cl_2 + 5AgNO_3 + 3H_2O = 5AgCl + HClO_3 + 5HNO_3.$$

There is no known remedy in this latter case; the error may be avoided only by shielding the precipitate from the action of direct sunlight or from powerful sources of artificial light.

Lundell and Hoffman also found that samples of dry silver chloride showed losses of 0.0001 to 0.0009 g. after exposure for 2-7 hours to strong illumination. Greater losses were observed for moist precipitates exposed to the action of light.

The excess of acid is removed by careful evaporation. Care must be taken not to fuse the precipitate because on fusion silver chloride is reduced by the organic matter remaining in the precipitate and low results are inevitable. Perfectly pure silver chloride, however, in the absence of reducing material may be fused without loss. A filtering crucible is always recommended for this precipitate because a paper filter is inconvenient and its use may lead to inaccurate results.

Since there are no sources of error that cannot be practically eliminated, this method for the determination of chloride ion is capable of higher precision than any other gravimetric precipitation method, and it is used, therefore, in atomic weight work.

Other Applications. This method serves for the determination of silver and for its separation from other metals; it may be applied also to the determination of any ion, the silver salt of which is insoluble in dilute nitric acid as chloride, bromide, iodide, cyanide, and thiocyanate ion. The solubility of these salts in mg. per 100 ml. of water at 20° C. is as follows: [1]

AgCl	0.14	AgCN	.02
AgBr	.008	AgCNS	.013
AgI	.0003		

The anion in any of the oxygen acids of the halogens, namely, hypochlorite, chlorite, chlorate, perchlorate, hypobromite, bromate, hypoiodite, iodate, and periodate ion, may be determined, after reduction to the corresponding halide, by precipitation as the silver halide in dilute nitric acid solution. Sulfurous acid is a satisfactory reducing agent for all of these oxygen acids except for perchloric acid upon which it is without action.

Interfering Substances. If any of the five ions just mentioned is being determined, the other four must obviously be absent. If silver is being determined, only mercurous salts interfere, as lead chloride is not precipitated in hot, dilute solution.

Procedure. Prepare filtering crucibles as directed on p. 30, dry them in the oven at 110°-120° C., cool and weigh them.

Weigh out samples of about 0.5 g. into 250 ml. beakers. Dissolve the solid in a little water, dilute the solution to about 150 ml., and add to it 10 drops of concentrated nitric acid. Without heating the solution, add 0.5 *M* silver nitrate slowly, with constant stirring (Equation (1)). After 10 ml. of the reagent has been added, allow the precipitate of silver chloride to settle and then test the supernatant liquid for complete precipitation by the addition of a few drops of silver nitrate. Test the liquid in this way after the addition of each 2 or 3 ml. of the precipitating agent until no further precipitate is produced. A sample weighing 0.5 g. should not require more than 20 ml. of 0.5 *M* silver

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[1] International Critical Tables, 6, 256.

nitrate. Heat the solution nearly to boiling, while stirring constantly, and hold it at this temperature until the precipitate coagulates and the supernatant liquid is clear. Do not expose the precipitate too much to bright light. Vigorous stirring of the solution greatly hastens the coagulation of the precipitate. The method, often recommended, of carrying out the precipitation in a conical flask which can be stoppered and shaken, is very effective. As soon as the solution clears, test the supernatant liquid again with a small quantity of silver nitrate to make certain that precipitation is complete; then decant the solution through a weighed filtering crucible. Add about 25 ml. of cold, very dilute nitric acid—0.5 ml. or 8 drops of the concentrated acid to 200 ml. of water—to the precipitate in the beaker (why is this used?), stir the mixture thoroughly, let it settle, and decant the supernatant liquid through the filter. Wash the precipitate four or five times in this way; then transfer it to the filtering crucible, and wash it with dilute nitric acid until the filtrate gives no test for silver ion. At least 10 washings will be required. (Why is a hot wash solution not used?) The nature of the precipitate is such that it may be more thoroughly washed by stirring it with dilute nitric acid in the beaker; hence this method is adopted for the first few washings. The filtering crucibles are placed on the bottom of a 400 ml. or 600 ml. beaker, which is then covered with a watch glass and placed in the electric drying oven for several hours, or over night if desired. Silver chloride may be fairly well dried at 110-120° C., but, if convenient, a higher temperature later is desirable. Gradual heating is essential. Otherwise the precipitate contracts so rapidly that water is trapped in the pores and can not be driven out without fusion. Silver chloride fuses at 455° C.; it should not be fused, however, unless the complete absence of organic matter is assured, and even then not in a filtering crucible.

The disadvantages of a paper filter, which have already been mentioned, are so pronounced, that details for this procedure will not be given, particularly in view of the fact that filtering crucibles are so commonly used.

Calculation of Results. Calculate the percentage of chlorine from the weight of silver chloride according to the method given in the preceding chapter. The factor for converting silver chloride into chlorine is 0.24738.

REVIEW QUESTIONS AND PROBLEMS

1. A sample of impure sodium bromate weighing 1.0750 g. is reduced to bromide and precipitated as silver bromide, which weighs 1.2100 g. Calculate the percentage of sodium bromate. *Note.*—Do not calculate the weight of sodium bromide.

2. A sample weighing 1.0820 g. of sodium phosphate containing water of crystallization is precipitated as silver phosphate, which is converted into silver chloride, weighing 0.5800 g. Calculate the percentage of Na_2HPO_4 present. *Note.*—Do not calculate the weight of silver phosphate. See rule 3, p. 310.

3. A certain weight of arsenic was precipitated as arsenious sulfide, which was dissolved in nitric acid and the arsenic acid precipitated as silver arsenate. The latter was converted into silver bromide, which weighed 1.1268 g. Calculate the weight of arsenic present. *Note.*—Do not calculate the weight of the sulfide or arsenate. See rule 3, p. 310.

Ans. 0.1498 g.

4. The halogens in 1.000 g. of a mixture of chloride and bromide are precipitated as silver bromide and chloride which together weigh 1.8500 g. Upon heating in chlorine, the silver bromide is converted into silver chloride, the loss in weight being 0.2000 g. Calculate the per cent of chlorine and of bromine in the sample.

Ans. 35.94 per cent Br and 24.87 per cent Cl.

5. The chlorine in a sample weighing 1.0000 g. is precipitated as silver chloride. Because of exposure to light this precipitate contains 0.0100 g. of silver and 0.9900 g. of silver chloride. What error in the percentage of chlorine in the sample is made by assuming it is all silver chloride?

6. One gram of a mixture containing only sodium chloride and iodide yields 1.8320 g. of mixed silver chloride and iodide. What is the percentage of each salt in the original mixture?

Ans. 30.00 per cent NaCl and 70.00 per cent NaI.

7. In problem 6 what would be the loss in weight if all iodide were changed to chloride by heating in chlorine?

8. In what proportions should anhydrous barium chloride and sodium chloride be mixed to give a material containing 40.00 per cent of chlorine?

9. What weight of silver chloride will be formed by the addition of excess of silver nitrate to 10.00 ml. of hydrochloric acid, specific gravity 1.098, containing 20.00 per cent HCl by weight?

10. What is the weight of pure silver nitrate required to precipitate the bromine in 2.000 g. of a mixture containing 60 per cent NaBr, 20 per cent KBr and 20 per cent NH_4Br?

11. The cyanide in a sample of potassium cyanide weighing 1.2070 g. was precipitated as silver cyanide and ignited to metal, which weighed 1.9800 g. Calculate the percentage of potassium cyanide in the sample.

Ans. 99.00 per cent.

12. A solution of ferric chloride is reduced to ferrous chloride by passing it through spongy silver in a silver reductor. It recuires 20.00 ml.

of 0.1000 *N* oxidizing agent to titrate the ferrous salt. How much silver was theoretically converted to chloride?

DETERMINATION OF SULFURIC ANHYDRIDE (SO_3) IN A SOLUBLE SULFATE

Principle. The sulfate is dissolved in water or in dilute hydrochloric acid, and the sulfate ion is precipitated as barium sulfate by the slow addition of barium chloride to a hot solution containing only a slight excess of free acid.

(1) $K_2SO_4 + BaCl_2 = \downarrow BaSO_4 + 2KCl.$

The precipitate is filtered, washed with water, carefully ignited at a red heat, and weighed as barium sulfate. From the weight of precipitate the percentage of sulfur trioxide is calculated.

Errors. 1. Barium sulfate is appreciably soluble in hydrochloric acid unless the latter is very dilute. Therefore, although the precipitation should be made in acid solution (why?), a large excess of acid must be avoided. The following figures show how large this error may be. At 26° C. the solubility of barium sulfate in 100 ml. of solution is as follows: in water, 0.3 mg.; in 1 *N* hydrochloric acid, 8.9 mg.; in 2 *N* hydrochloric acid, 10.1 mg.; in 2 *N* nitric acid, 17 mg., but it is much less in the presence of excess barium ion.

2. Barium sulfate shows a great tendency to carry down other salts and is therefore practically never obtained pure. Whether the results will be high or low will depend on the nature of the salt present as an impurity in the precipitate, and, when sulfate is being determined, accurate results are usually due to a compensation of errors.

Foreign anions, such as chloride, nitrate and chlorate are coprecipitated as the corresponding barium salts and form an addition to the true weight of the sulfate. Therefore, this error will cause high results when sulfate is being determined; the nitrate is converted to oxide on ignition. In the case of the chloride, this error is avoided fairly well by very slow addition of barium chloride to the solution, which is being stirred constantly; in the case of the nitrate and chlorate the error cannot be avoided and therefore these ions must always be removed by evaporation with a large excess of hydrochloric acid.

Foreign cations such as the alkali metals, calcium and ferric iron are coprecipitated, forming a precipitate that is made up to a certain extent of occluded foreign sulfate, e.g. K_2SO_4. If this is not changed on ignition the results will, nevertheless, be low if sulfate is being determined, because the equivalent weight of the foreign cation will be less than that of barium, and the magnitude of the error will depend upon the difference between the weight of its sulfate and that of an equivalent amount of barium sulfate. If the foreign sulfate is decomposed on ignition, the error will be still greater, as, for example, if ammonium sulfate is present, all of which is lost, or ferric sulfate, which loses sulfur trioxide to form ferric oxide. Thus, a given amount of sulfur in the form of sodium sulfate will weigh about six-tenths as much as it would in the form of barium sulfate. This error cannot be entirely avoided except by removal of the interfering ions. Ferric ions may be precipitated or reduced to the ferrous form which is not co-precipitated in this process to any great extent; sodium and potassium ions cannot be readily removed. Dilution of the solution will decrease the error. Popoff and Neuman[1] have shown that by adding the sulfate to the barium solution, errors of the last type are greatly reduced, but errors due to anions are increased. Reprecipitation, which is the usual method of purifying a precipitate, is, unfortunately, not applicable to barium sulfate, because it is so nearly insoluble in all suitable reagents. It may be transposed by fusion with sodium carbonate, but the process is tedious.

A large amount of work has been published on the errors involved in the precipitation of barium sulfate.[2]

3. Barium sulfate is easily reduced at a high temperature to barium sulfide by the carbon of the filter paper:

$$(2)\quad BaSO_4 + 4C = BaS + 4CO.$$

Reduction may be completely avoided by burning off the carbon at as low a temperature as possible—not above a faint red heat.

If barium is being determined, the errors due to foreign anions

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[1] Popoff and Neuman, Ind. Eng. Chem. Anal. Ed. **2**, 45 (1930).

[2] For an extensive discussion of this subject see Kolthoff and Sandell, Textbook of Quantitative Inorganic Chemical Analysis, Macmillan, 1936, p. 309.

and to reduction are readily eliminated by moistening the precipitate with a drop of sulfuric acid and igniting.

Other Applications. This method may be reversed and used for the separation and determination of barium. It may also be used for the separation and determination of lead and of strontium; the sulfates of these metals are more soluble than is barium sulfate ($PbSO_4$, 4.1 mg., and $SrSO_4$, 15.4 mg. per 100 ml. at 25° C.) and special precautions are therefore necessary in their precipitation and washing. In the case of strontium sulfate, alcohol must be added to the solution to reduce the solubility of the precipitate. The determination of lead as the sulfate is described later under the analysis of brass. This sulfate precipitation method not only serves to separate barium, strontium, and lead from those metals forming soluble sulfates, but also to separate the sulfate ion from other ions not precipitated under the conditions used. Sulfur in any form, such as a sulfide, sulfite, thiosulfate, tetrathionate, or persulfate, may be converted to the sulfate and be determined by this method. Lead sulfate may be separated fairly well from barium sulfate by dissolving the former in a solution of ammonium or sodium acetate containing a little sulfate.[1]

Procedure. Weigh out three samples of about 0.5 g. (between 0.5 and 1 g.) into 400 ml. beakers, add 15 ml. of water and heat the mixture. If the sample is insoluble in water, add concentrated hydrochloric acid carefully, drop by drop, until a solution is obtained; then add 0.5 ml. of acid (8 drops) in excess. If the sample is soluble in water, add 0.5 ml. of concentrated hydrochloric acid to the solution. Dilute to 200-250 ml., cover the beaker with a watch glass, heat the liquid to boiling, and add 0.25 *M* barium chloride—61 g. of $BaCl_2 \cdot 2H_2O$ per liter—drop by drop while stirring the solution constantly. Keep the solution just at the boiling point. Continuous stirring is necessary to prevent bumping while heat is being applied. The reagent is most conveniently added from a buret held by a clamp in a slanting position so that the drops will run down the side of the beaker. (Why is the barium chloride added so slowly?) After adding 20 ml. of barium chloride solution, let the precipitate settle for a minute or two. Then test the supernatant liquid for

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[1] Marden, J. Am. Chem. Soc. 38, 310 (1916).

complete precipitation with a drop or two of the reagent. If a precipitate is formed, add slowly 5 ml. more of the reagent and test again; repeat these operations until there is an excess of the precipitating agent present. Do not let the volume of the solution fall below 150-200 ml.; add water if necessary. Keep the solution hot for 1 hour to allow time for complete precipitation of all of the barium sulfate, the last traces of which do not separate immediately. Do not attempt to hold the solution at the boiling point. Keep the beakers covered with watch glasses at all times, and when removing the cover always rinse off the under side of it into the beaker with a jet of water from the wash bottle. Do not place the covers on the desk, where they will collect dirt; if this is done, they must be rinsed off with distilled water before replacing them on the beakers. The precipitate should settle readily and a clear, supernatant liquid be obtained —an indication that slow precipitation has given a coarse-grained precipitate. As the hot solution stands the crystals tend to become somewhat purer. (See p. 300.)

If at the end of 1 hour (longer heating is not harmful) the clear, supernatant solution gives no precipitate upon the addition of a drop or two of barium chloride, the barium sulfate is ready to be filtered. Without disturbing the precipitate, decant the supernatant solution through the ashless filter. Test the filtrate with a few drops of barium chloride; if no precipitate forms, discard the liquid, rinse out the beaker and place it again under the funnel. If a precipitate forms, the entire sample must be thrown away and a new one started, for the precipitation was incomplete. The object of discarding the filtrate at this point is to avoid the necessity of refiltering the entire solution if any precipitate should run through the filter. Transfer the precipitate to the filter with a jet of hot water from the wash bottle. If any of the precipitate has run through the paper, pour a little filter paper pulp on to the filter, and pour the solution back through the filter after placing a clean beaker under the funnel. Repeat this operation until a clear filtrate is obtained. If the process was properly carried out, such trouble will never be experienced. Examine the beaker and stirring rod carefully to be sure that all of the precipitate has been transferred to the filter. With a rubber-tipped rod (called a "policeman") rub loose any precipitate that adheres to the beaker or stirring rod, and transfer this to the filter. Wash the precipitate 10 times with hot water. Direct the jet as near the top of the paper as possible and let each portion of wash solution run through before adding the next. Then test a few ml. of the washings for chloride ion with silver nitrate. If a test is obtained, continue washing the precipitate until the filtrate is free from chloride ion, an indication that all soluble salts have been removed.

Wrap up the precipitate by folding over the edge of the filter paper, remove the paper carefully from the funnel and place it in a porcelain crucible previously ignited and weighed without the cover. Any precipitate which adheres to the funnel should be wiped off with a small piece of ashless filter paper which is then added to the crucible. Place the crucible on a triangle several centimeters above a small flame and dry the filter. Then lower the crucible, which may be covered or uncovered, to within 1 cm. of the flame, and char the paper below a red heat. When the paper is charred in this way, it can be burned afterwards at a lower temperature. Smoke and volatile matter will be given off, some of which will condense on the cover, if one is used, but any deposit there may be disregarded. If the temperature rises to a red heat, some of the barium sulfate may be reduced to barium sulfide. After the paper has been charred, lower the *uncovered* crucible until the bottom becomes dull red and burn off all the carbon of the filter. Place the crucible in a slanting position so as to allow free access of air. When the precipitate is white, lower the crucible until it attains a red heat, and ignite thus for about 10 minutes. Allow the crucible to cool somewhat, transfer it to the desiccator, and, when cold, weigh the barium sulfate.

The tarry matter may be removed from the cover by placing it, clean side down, on a triangle, and heating it for some time.

The ash of the filter paper is negligible, as the paper has been freed from nearly all mineral matter by treatment with hydrochloric and hydrofluoric acids. Be sure that only this kind of paper is used.

The barium sulfate may be filtered through a Gooch crucible if desired.

Calculate the percentage of sulfur trioxide in the sample. The factor for converting barium sulfate into sulfur trioxide is 0.3430.

Review Questions and Problems

1. Explain the error produced in the determination of sulfate by the coprecipitation of each of the following with the barium sulfate: sodium sulfate, ammonium sulfate, barium chlorate, ferric sulfate.

2. What will be the error in the determination of sulfur trioxide in a 1.0000 g. sample if the barium sulfate, assumed to be pure, actually contains, before ignition, 10.0 mg. of ammonium sulfate?

3. What will be the error in problem 2 if the impurity is 10.0 mg. of barium nitrate?

Ans. + 0.201 per cent.

4. The sulfur dioxide in 20 liters of air is absorbed in alkaline hydrogen peroxide and precipitated as barium sulfate, which weighs 0.0423 g. Calculate the per cent by volume of sulfur dioxide in the air if 1 ml. of the former weighs 2.90 mg.

Ans. 0.0200 per cent.

5. The weight of a sample is 0.5650 g. and the weight of barium sulfate obtained from it is 1.4005 g. Calculate the per cent of FeS_2 in the sample.

6. The weight of a sample is 0.6240 g. and the weight of barium sulfate obtained from it is 1.0504 g. Calculate the percentage of $Fe_2(SO_4)_3$ in the sample.

7. The sulfur in 1.1909 g. of the pure sodium salt of a complex thionic acid, $Na_2S_xO_6$, is converted into barium sulfate, which weighs 3.5013 g. Calculate the value of x.

Ans. 3.0.

8. How much crystallized barium chloride, $BaCl_2 \cdot 2H_2O$, would be required to precipitate the sulfate in 1.0000 g. of ammonium ferrous sulfate, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$?

9. Suggest a method for determining barium and lead in an alloy of these two metals.

10. Suggest a method for determining sulfate in an insoluble sulfate such as barium sulfate.

11. One gram of pure ferrous sulfide is ignited to ferric oxide. Calculate the loss in weight.

DETERMINATION OF MAGNESIUM OXIDE IN A MAGNESIUM COMPOUND

Principle. The substance is dissolved in water or in dilute hydrochloric acid. To this acid solution ammonium phosphate is added; no precipitate is formed if enough acid is present. The magnesium is then precipitated as coarsely crystalline magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, by adding an excess of concentrated ammonia slowly to the cold solution.

$$(1)\quad MgO + 2HCl = MgCl_2 + H_2O.$$

$$(2)\quad MgCl_2 + (NH_4)_2HPO_4 + NH_4OH = \downarrow MgNH_4PO_4 + 2NH_4Cl + H_2O.$$

Due to its greater solubility this precipitate forms more slowly than does barium sulfate; therefore the solution should stand for a considerable time before being filtered. The precipitate is washed with cold, dilute ammonium hydroxide—one part of strong ammonia to nineteen parts of water—to decrease its solubility, and also to prevent hydrolysis of the double phosphate. The magnesium ammonium phosphate is then ignited at a bright red heat (1000°-1100° C.) to magnesium pyrophosphate, $Mg_2P_2O_7$,

$$(3)\quad 2MgNH_4PO_4 \text{ (ignited)} = Mg_2P_2O_7 + 2NH_3 + H_2O$$

and is weighed as such. A double precipitation is required for very precise results.[1]

Errors. 1. Magnesium ammonium phosphate is considerably more soluble than most of the precipitates used in quantitative analysis. To reduce its solubility, a common ion must be added to the wash liquid—either magnesium, phosphate, or ammonium ion. Since both phosphate and ammonium ions are present in excess in the solution, the precipitation is complete and no trouble would be experienced if dilute ammonium phosphate could be used as a wash solution. It is impossible, however, to do this since this salt is not volatile but leaves on ignition a residue of metaphosphoric acid, HPO_3. Only the ammonium ion, therefore, is available for reducing the solubility of the precipitate. Ammonium nitrate is not satisfactory because it does not prevent the hydrolysis of the precipitate:

$$(4)\quad MgNH_4PO_4 + H_2O = MgHPO_4 + NH_4OH.$$

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[1] This subject has been carefully studied by Epperson, J. Am. Chem. Soc. **50,** 321 (1928) and by Hoffman and Lundell, J. Research Natl. Bur Standards **5,** 279 (1930).

Although the presence of magnesium acid phosphate, $MgHPO_4$, would not affect the ultimate composition of the ignited precipitate, this acid phosphate, since it contains no common ammonium ion, is more soluble in solutions of ammonium salts than is the double phosphate. Ammonium hydroxide not only contains the necessary common ion but prevents the hydrolysis of the precipitate, since it is one of the products of hydrolysis. The following figures [1] will serve to illustrate this point:

Solvent	$MgNH_4PO_4 \cdot 6H_2O$, grams, dissolved in 100 ml. of solvent at 20° C.
Water	0.0516
5 per cent NH_4Cl	.1055
1.1 N NH_4OH	.0098
1.1 N NH_4OH + 5 per cent NH_4Cl	.0165
1.1 N NH_4OH + 10 per cent NH_4Cl	.0541

It is evident from these figures that the solubility loss may be quite appreciable if excessive amounts of wash solution are used. Each 100 ml. of 1.1 N ammonium hydroxide according to the data just given would dissolve 1.6 mg. of magnesium oxide. In the wash solution used the solubility may be less, and it may be still further decreased by cooling the solution. This error due to solubilty of the precipitate can, therefore, be reduced by cooling the wash solution and using as little of it as necessary.

2. Potassium ions, if present in the solution, will replace the ammonium in the double phosphate to some extent, and sodium may be coprecipitated. Such a precipitate on ignition can not be entirely converted into magnesium pyrophosphate, and high results are obtained. A second precipitation eliminates this error in the case of the sodium ion but not when much potassium is present.

3. The presence of a large excess of ammonium hydroxide or of ammonium salts causes high results, probably due to the coprecipitation of ammonium phosphate, which on ignition forms metaphosphoric acid, HPO_3. Some authors claim that this error is due to the presence of another double phosphate,

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[1] Wenger, Dissertation, Geneva, 1911.

$(NH_4)_4Mg(PO_4)_2$, which, on ignition, forms the metaphosphate, $Mg(PO_3)_2$. Reprecipitation eliminates this error. Moderate amounts of a citrate have no harmful effect, but oxalate delays precipitation and in some cases causes it to be incomplete. This is due to the formation of a complex oxalate.

4. The addition of the phosphate ion to the ammoniacal solution causes the results to be high and the error is often very serious. Reprecipitation under proper conditions does not entirely remedy this error, but usually causes the results to be low. There is, however, no excuse for carrying out the precipitation in this way, although this procedure has been recommended by some authors.

5. If the ignition is not properly conducted, the precipitate may be slightly reduced by the carbon of the filter paper. The use of a filtering crucible avoids this trouble, but a paper filter gives very satisfactory results.

6. When an ammoniacal solution remains for a considerable time in a glass vessel, the latter is attacked somewhat, silica dissolves, and is often carried down by the precipitate. This effect is seldom serious.

7. The precipitate shows a great tendency to adhere to the glass if this has been scratched. A new beaker is most satisfactory, and care should be taken not to scrape it with a glass rod.

Other Applications. Certain other metals form similar insoluble double ammonium phosphates. Those of magnesium and manganese, being insoluble in ammonia, are precipitated in an ammoniacal solution; those of cadmium, zinc, and cobalt are soluble in ammonia and must, therefore, be precipitated in a neutral solution and be washed with water instead of with ammonium hydroxide. This procedure can be followed without serious loss of precipitate, since these double phosphates are so much less soluble than the corresponding magnesium salt that a special wash solution is not required to prevent their hydrolysis. All of these phosphates are readily soluble in dilute acids. All except the magnesium salt are usually precipitated in hot solution. Manganese, zinc, cadmium, and cobalt ions are precipitated first as simple phosphates which later become the double salts; heat hastens this change. This method will be applied to the determination of zinc in brass. All common metals except the alkalis form insoluble phosphates, but only the five mentioned readily form double salts. Magnesium may also be precipitated as magnesium ammonium arsenate, $MgNH_4AsO_4$.

It might appear that magnesium could be separated from zinc and cadmium by this method because the latter two phosphates are soluble in ammonia. Such a separation, however, is not possible.

Interfering Substances. Since all the common metals except arsenic, potassium and sodium, and the ammonium ion, form insoluble phosphates, this method can not be used as a separation, but is applied to the determination of any of the metals mentioned above only after the removal of all others.

Procedure. Weigh out three samples of approximately 0.5 g. each into 250 ml. beakers, add 15 ml. of water, and cover the beaker with a watch glass. Then add 5 ml. of concentrated hydrochloric acid, and heat the material, if necessary, to obtain complete solution. Rinse off the cover and sides of the beaker, dilute the solution to 150 ml., and cool to room temperature (Equation (1)). Add to the cold, acid solution about 2 g. of ammonium phosphate, $(NH_4)_2HPO_4$, dissolved in a little water. No precipitate should appear. Add a few drops of methyl red as an indicator. To the clear, acid solution, cooled in ice water, add, drop by drop with constant stirring, a filtered solution of concentrated ammonia, until the indicator turns yellow. Avoid as far as possible touching the rod to the sides of the beaker. Add 5-10 ml. of concentrated ammonia to the solution, stir it for a few minutes and allow it to stand in a cold place at least 4 hours or overnight if preferred. The crystalline precipitate will, in spite of the above precautions, adhere somewhat to the sides of the beaker and to the stirring rod, which should, therefore, be left in the solution.

Decant the supernatant liquid through a filter, or through a filtering crucible, and discard the filtrate. Transfer the precipitate to the crucible. Rub loose with a rubber-tipped rod all the precipitate adhering to the beaker and the stirring rod, and transfer the material to the filter. Wash the precipitate with cold (why?) dilute ammonium hydroxide—one part of filtered, strong reagent ammonia to nineteen of water—(why is this used?), until a few ml. of the filtrate, when acidified with nitric acid and tested with silver nitrate, gives no test for chloride ion. At least 8 or 10 washings will be required. Use as little wash solution as necessary (why?) and apply it in small portions; direct the jet around the edge of the filter. Dry the filtering crucible containing the precipitate in the oven or above a very low flame. When the precipitate appears dry, place the filtering crucible inside another porcelain crucible, apply heat slowly at first, and then at the full temperature of a good burner—bright red—for an hour. Cool and weigh the filtering crucible and contents. Ignite the material again for half-hour periods until the loss in weight is not more than 0.3 mg. With a temperature of 1000° C., constant weight is very readily obtained. Ignition in an electric muffle is the most desirable method.

If a paper filter is used, either separate the dried precipitate from the paper and destroy the paper first in a weighed crucible, or else transfer the precipitate and paper to the weighed crucible. If the precipitate is to be separated from the paper, transfer it to a clean watch glass placed upon black glazed paper, and cover it with a clean, dry beaker while the paper is being destroyed. In either case char the paper by using a very low flame under the open crucible; after the ammonia has been expelled from the precipitate at a temperature below red heat, burn off the carbon at a moderate red heat while keeping the crucible in a slanting position to allow free access of air. If the precipitate has been separated from the paper, cool the crucible after the paper has been destroyed and transfer the main bulk of the precipitate to the crucible, using a brush with ashless fibers to transfer the particles that adhere to the glass. After the ammonia has been expelled and when the precipitate is nearly white or gray (it is almost never white), ignite it for one-half hour at a bright red heat (1000° 1100° C.). Cool and weigh. Ignite the material again for half-hour periods until the weight is constant to within 0.2-0.3 mg.

If there is time for a second precipitation, the results will be more accurate because of the closer control of the excess of reagents present. In this case the first precipitate should always be filtered through a paper filter. Dissolve the precipitate in 50 ml. of warm, 1.1 *N* hydrochloric acid—one part of the concentrated acid to nine parts of water—wash the paper thoroughly with hot 0.1 *N* hydrochloric acid, and dilute the solution thus obtained to 125 or 150 ml. Add 0.25 g. of diammonium phosphate, cool the liquid in ice water and again precipitate the magnesium by the above procedure. Allow the solution to stand 4 to 24 hours; then filter through a filtering crucible or a paper filter and ignite the precipitate as has been directed.

Calculate the percentage of magnesium oxide from the weight of magnesium pyrophosphate thus obtained. The conversion factor is 0.3621.

DETERMINATION OF PHOSPHORIC ANHYDRIDE (P_2O_5) IN A SOLUBLE PHOSPHATE

Principle. Magnesium ion may be used in the presence of ammonium ion to precipitate a phosphate or an arsenate, and this method is the usual gravimetric one for determining phosphorus or arsenic in the absence of interfering substances. Arsenic acid is very similar to phosphoric acid in its reactions; the double ammonium arsenate formed is of the same type as the double ammonium phosphate. Thus ammonium arsenate could have been used in the determination of magnesium, to form magnesium ammonium arsenate, $MgNH_4AsO_4 \cdot 6H_2O$, which is changed to the pyroarsenate, $Mg_2As_2O_7$ on ignition. If arsenic is being determined, it is converted first into arsenic acid, H_3AsO_4, by a suitable oxidizing agent, such as nitric acid. Then after the addition of magnesium chloride and ammonium chloride or acetate to the solution, magnesium ammonium arsenate is precipitated by ammonia as directed later for a phosphate.

The process for a phosphate is similar to that used in determining magnesium. Ammonium hydroxide is added to the cold, acid solution containing the phosphate, magnesium and ammonium salts. The precipitate of magnesium ammonium phosphate is filtered, preferably through a filtering crucible, is washed with cold, dilute ammonia, and ignited in an oxidizing atmosphere at a bright red heat (1000°-1100° C.).

The errors of this process have already been discussed under "Determination of Magnesium Oxide."

Interfering Substances. Arsenic acid must be absent. It may be removed by precipitation as arsenic sulfide from a strong hydrochloric acid solution, or by one or two evaporations to dryness, after a preliminary reduction of all arsenic to arsenious acid by means of sulfur dioxide and after the addition of a little hydrobromic acid and a large excess of concentrated hydrochloric acid. The arsenic is volatilized as arsenic trichloride. Any other acids which form insoluble magnesium salts will obviously interfere. The common acids may, therefore, be present. All other metals except the alkalis form insoluble phosphates and must for this reason be absent. When this method is to be applied to the determination of phosphate ion in calcium phosphate (phosphate rock), the phosphorus is first precipitated in a nitric acid solution as ammonium phosphomolybdate to separate it from other metals. This precipitate is dissolved in ammonia with the formation of ammonium phosphate and ammonium molybdate. The phosphate is then precipitated with a magnesium salt, the molybdate not interfering when proper conditions are chosen.

Procedure. Weigh out three samples of about 0.5 g. each into unscratched 250 ml. beakers, add 15 ml. of water and 5-10 ml. of concentrated hydrochloric acid to the mixture, and dilute the solution to 125-150 ml. Add a few drops of methyl red as indicator, 10-20 ml. of magnesia mixture (see directions below for preparation of this) for each 0.1 g. of P_2O_5 present, and cool the solution in ice water. Then add filtered, concentrated ammonium hydroxide slowly with vigorous stirring until the solution is slightly alkaline. Stir the liquid for a few minutes or until the precipitate is well formed, and then add 5 to 10 ml. of filtered, concentrated ammonium hydroxide. Let the solution stand at least 4 hours and preferably over night. Filter the precipitate through a filtering crucible, and wash it with cold dilute ammonium hydroxide—one part of the concentrated reagent to nineteen of water. Dry the precipitate in the oven for an hour or more, place the filtering crucible inside another porcelain crucible, and apply heat slowly at first and then at the full temperature of a good burner of the Meker type (1000°-1100° C.) for an hour. Cool and weigh the crucible and residue. Subsequent ignitions should cause a loss in weight of not more than 0.3 mg. The precipitate of magnesium pyrophosphate, $Mg_2P_2O_7$, is rarely pure white; it is usually gray.

The magnesia mixture is prepared as follows: Dissolve 50 g. of magnesium chloride, $MgCl_2 \cdot 6H_2O$, and 100 g. of ammonium chloride in 500 ml. of water. Make the solution slightly ammoniacal, allow it to stand over night, and then filter it. Acidify the filtrate with hydrochloric acid, and add 5 ml. excess of concentrated hydrochloric acid. Dilute the solution to 1 liter.

The precipitate of magnesium ammonium phosphate may also be filtered through paper and be ignited in a porcelain crucible as directed under the "Procedure for Magnesium."

If any of the precipitate adheres to the beaker or stirring rod so firmly that it can not be wiped off, dissolve it in a few drops of concentrated hydrochloric acid. To this solution add a few ml. of magnesia mixture and reprecipitate the magnesium ammonium phosphate in a very small volume. Filter the precipitate through a 5.5 cm. ashless filter, then ignite it in a small crucible, and brush all residue carefully into the crucible containing the main precipitate. Such a procedure is rarely necessary.

If there is time for a second precipitation, the results will be more accurate because the precipitate will then have the correct composition. In this case the first precipitate should always be filtered through a paper filter. Dissolve the precipitate in 50 ml. of warm 1.1 *N* hydrochloric acid—one part of the concentrated acid to 9 parts of water—wash the paper thoroughly with hot 0.1 *N* hydrochloric acid and dilute the solution to 125 or 150 ml. Add 1 to 3 ml. of magnesia mixture. Cool the liquid in ice water and again precipitate the phosphate by the above procedure. Allow the solution to stand from 4 to 24 hours; then filter through a filtering crucible or a paper filter and ignite the precipitate as directed above.

Calculate the percentage of phosphorus pentoxide from the weight of magnesium pyrophosphate obtained. The factor for converting the pyrophosphate into the pentoxide is 0.6379.

DETERMINATION OF PHOSPHORIC ANHYDRIDE IN PHOSPHATE ROCK

Principle. Phosphate rock consists principally of calcium phosphate with notable amounts of fluorine and smaller amounts of carbonate, silicate, iron, aluminum and magnesium. It is dissolved in nitric acid, the silica removed and the fluorine converted into harmless fluoboric acid, HBF_4, by the addition of boric acid. The phosphorus is separated from interfering elements such as calcium, iron and aluminum by precipitating it as ammonium phosphomolybdate, $(NH_4)_3PO_4 \cdot 12MoO_3$. This is dissolved in ammonia, precipitated as magnesium ammonium phosphate and the latter ignited to pyrophosphate. In less accurate work the phosphomolybdate is weighed or titrated with sodium hydroxide:

$$(5)\quad (NH_4)_3PO_4 \cdot 12MoO_3 + 23NaOH = NaNH_4HPO_4 + 11Na_2MoO_4 + (NH_4)_2MoO_4 + 11H_2O.$$

Procedure.[1] Weigh out 0.5 g. samples[2] of the well-ground and dried material into 150 ml. beakers and add 5 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid. Evaporate the solution to a syrupy consistency on a low temperature hot plate, add 0.2 g. of boric acid and dissolve the residue in a mixture of 1 ml. of concentrated nitric acid and 10 ml. of water. Heat to boiling and filter through a small filter into a 250 ml. beaker. Wash with small portions of cold water using 50 ml. in all.

To the combined filtrate and washings add 15 ml. of concentrated nitric acid and nearly neutralize the solution with ammonia, as shown by the appearance of a slight permanent precipitate. Heat the solution to 60° C., add 125 ml. of molybdate reagent, stirring with a thermometer, and maintain the solution at 60° C. for half an hour with frequent stirring. Then allow it to stand four hours at room temperature. Filter and wash five or six times by decantation with 5 per cent ammonium nitrate solution. Set the beaker containing most of the precipitate beneath the funnel containing the filter and dissolve the precipitate by pouring through the filter successive portions of 20 ml. of a solution prepared by dissolving 5 g. of citric acid in 140 ml. of water and adding 70 ml. of concentrated ammonium hydroxide. Wash the filter with several portions of hot 0.5 *N* ammonium hydroxide (one volume of concentrated ammonia water to 20 volumes of water), then with hot water and finally with hot dilute hydrochloric acid (one volume of concentrated acid to 20 of water). The volume of the solution should be 100-150 ml., never more than the latter. Add methyl red indicator, neutralize the solution with concentrated hydrochloric acid,

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[1] Lundell and Hoffman, J. Assoc. Off. Agr. Chem. 8, 184 (1924).

[2] Samples weighing 0.25 g. may be used if preferred, in which case 75 ml of molybdate reagent to be added later will be sufficient.

add 1 ml. in excess, and then 10 ml. of magnesia mixture. Cool the solution in cold water and add concentrated ammonium hydroxide slowly with stirring until the solution is alkaline, then add 5 ml. more. Allow the precipitate to stand at least four hours, preferably over night.

Filter, wash with dilute ammonium hydroxide, dissolve and reprecipitate as previously directed under "Determination of Phosphoric Anhydride," p. 335, and weigh as magnesium pyrophosphate.

Calculate the percentage of phosphorus pentoxide.

Preparation of the molybdate reagent. Mix 100 g. of pure molybdic anhydride or an equivalent weight of molybdic acid (85 per cent MoO_3) with 400 ml. of water, and add 80 ml. of concentrated ammonia. When solution is complete, filter and pour the filtrate slowly, with stirring, into a cold mixture of 400 ml. of concentrated nitric acid and 600 ml. of water. Allow the solution to stand over night and filter.

REVIEW QUESTIONS AND PROBLEMS

1. A sample of phosphate rock weighing 0.5190 g. yielded 0.3050 g. of magnesium pyrophosphate. Calculate the percentage of P_2O_5 in the rock.

2. Give the formulas for ortho-, pyro-, and metaphosphoric acid, and show how the latter two acids are derived from the ortho- acid. How may they be converted into the ortho- acid? How is potassium pyrosulfate derived from the bisulfate? From the persulfate?

3. The precipitate of ammonium magnesium phosphate from a 1.0000 g. sample contains sufficient ammonium phosphate to give 10.0 mg. of metaphosphoric acid, HPO_3, on ignition. Calculate the error in the determination of magnesium oxide in the sample.

4. One gram of pure ammonium phosphomolybdate will yield how much magnesium pyrophosphate?

5. One liter of a saturated aqueous solution of magnesium ammonium arsenate, $MgNH_4AsO_4 \cdot 6H_2O$, contains at 20° C., 206.6 mg. of the salt. Express the solubility in terms of mg. of arsenic per liter.

6. A precipitate of pure magnesium ammonium phosphate is ignited and the ammonia collected in 50.00 ml. of 0.1000 N hydrochloric acid. The excess of acid required for titration 9.00 ml. of 0.1200 N alkali. Calculate the weight of magnesium oxide in the precipitate.
Ans. 0.1581 g.

7. Prove that in gravimetric analysis it is necessary to use a sample equal to the conversion factor in grams when it is desired that the grams

of precipitate multiplied by 100 shall equal the percentage of constituent sought.

8. Write equations for the gravimetric determination of manganese in potassium permanganate.

9. Outline a method for the analysis of an alloy of magnesium and cadmium.

10. Give the reactions involved in the determination of arsenic and phosphorus in a solution containing both arsenic and phosphoric acids.

DETERMINATION OF CALCIUM OXIDE IN CALCIUM CARBONATE

Principle. The sample is dissolved in dilute hydrochloric acid, and ammonium oxalate or oxalic acid is added to the acid solution; the calcium is then precipitated as calcium oxalate, $CaC_2O_4 \cdot H_2O$, by gradually neutralizing the acid with ammonia.

$$(1)\quad CaCO_3 + 2HCl = CaCl_2 + CO_2 + H_2O.$$

$$(2)\quad CaCl_2 + (NH_4)_2C_2O_4 = \downarrow CaC_2O_4 + 2NH_4Cl.$$

The crystalline precipitate is filtered and washed with hot 0.25 per cent ammonium oxalate solution to reduce its solubility. One hundred ml. of water at 18° C. dissolves 0.6 mg. of calcium oxalate, and at 95° C., 1.4 mg. In the presence of ammonium oxalate the solubility of the precipitate is practically zero. Calcium oxalate is soluble in acids to an extent depending on the concentration of hydrogen ion, but its solubility is not affected by an excess of ammonia.

When the precipitate is ignited, two reactions occur: the first is complete in 1 hour at 500° C.,

$$(3)\quad CaC_2O_4 \text{ (heated to 500° C.)} = CaCO_3 + CO,$$

the second is rapid at about 850° C., but begins at about 600° C.,

$$(4)\quad CaCO_3 \text{ (heated to 850° C.)} = CaO + CO_2.$$

To attain a temperature of 850° C. with gas in a porcelain crucible, the flame of the Meker burner must be enclosed in a small furnace. The precipitate is ignited to calcium oxide which is hygroscopic and which must, therefore, be weighed quickly.

Ignition to the oxide has certain disadvantages: the proper temperature is attained with difficulty in a porcelain crucible, although easily in a platinum crucible; the precipitate absorbs water and carbon dioxide rapidly from the air. Ignition to the carbonate has neither of these disadvantages, but it does call for a temperature between 475° and 525° C.[1] At 450° C. the decomposition of the oxalate is slow; 4 or 5 hours are required for the complete conversion into the carbonate. At 550° C. the carbonate loses some carbon dioxide. The dissociation of the carbonate is a true equilibrium reaction, but that of the oxalate is not. At 500° C. the dissociation pressure of calcium carbonate is 0.11 mm., a value less than the partial pressure of carbon dioxide in ordinary air. Therefore no dissociation of the carbonate will occur at this temperature. At 600° C. the dissociation pressure of calcium carbonate is 2.35 mm., and therefore carbon dioxide will slowly be lost. At 890° C. the dissociation pressure is 760 mm.

It is not difficult to maintain a temperature between 475° and 525° C. in an electrically heated muffle. When such apparatus is available, the calcium may be weighed more easily and accurately as calcium carbonate than as calcium oxide. This is particularly true if porcelain crucibles are to be used. In this case the oxalate must be filtered through a Gooch or porcelain filtering crucible, and not through paper. This method of weighing as carbonate is recommended because it has been found to give excellent results.

A method of determining calcium as calcium carbonate by heating the oxalate to about 700° C. in an atmosphere of carbon dioxide has been described by Foote and Bradley.[2] This technique requires special apparatus, and is, therefore, not so simple as that of heating the precipitate in air at a lower temperature. The atmosphere of carbon dioxide prevents the dissociation of calcium carbonate at the higher temperature.

Errors. Calcium oxalate carries down the alkali metals slightly. Magnesium may be coprecipitated to a considerable extent, the amount depending largely upon the time that the precipitate is in contact with the solution before filtration. All other metals must be absent. This error is reduced by precipitation in an acid solution, because in this way all but the last traces of precipitate are formed before the solution becomes neutral.

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[1] Willard and Boldyreff, J. Am. Chem. Soc. **52**, 1888 (1930).

[2] Foote and Bradley, J. Am. Chem. Soc. **48**, 676 (1926).

Such a procedure also causes the formation of a much coarser precipitate than that obtained by adding oxalate ion to the ammoniacal solution. (Why?) If much magnesium is present, a second precipitation may be required, and precipitation will be incomplete unless enough of the oxalate is added to combine with both calcium and magnesium.

The solubility of the precipitate is slight in cold water but quite appreciable in hot water. In cold solution the addition of a common ion in the form of ammonium oxalate reduces the solubility of the calcium oxalate practically to zero. Oxalic acid can not be used, because the common ion effect is more than offset by the solvent effect of the hydrogen ion, formed from the dissociation of the oxalic acid into H^+ and $HC_2O_4^-$.

If an excess of ammonia is added, there is the possibility that the glass will be attacked by the hot, alkaline solution and that the silica dissolved will contaminate the precipitate. Since this effect depends upon the concentration of ammonium hydroxide present, this error may be avoided by adding only enough ammonia to neutralize the solution or to make it slightly alkaline, and by not allowing an alkaline solution, especially if warm, to stand more than a few hours before filtration. If desired, an indicator such as methyl orange or methyl red may be used. Calcium oxalate may be completely precipitated from a solution having a *p*H of 4.

Calcium carbonate may contain a little calcium oxide if the temperature of ignition is too high, or a little of the oxalate if it is too low.

Since calcium oxide is not reduced by carbon, no special care is necessary in burning off the filter. Care must be taken, however, to maintain a very high temperature during ignition and to heat the material sufficiently long to decompose all calcium carbonate. This dissociation is assisted by the removal of the carbon dioxide. (How could the dissociation of calcium carbonate at 800° C. be prevented?)

Since calcium oxide absorbs moisture and carbon dioxide, it must not be allowed to stand in the desiccator too long and the weighing must be made quickly and in a covered crucible.

Other Applications. The calcium oxalate may be determined volumetrically instead of by ignition to the carbonate or oxide. Many other metals such as lead, copper, zinc, nickel, strontium, thorium may be precipitated as oxalates, but except in the case of some of the rarer elements this method is seldom used, as better methods are available.

Interfering Substances. All the common metals except the alkalis form insoluble oxalates. Magnesium oxalate is slightly soluble and its apparent solubility is greatly increased by its tendency to form supersaturated solutions and complex salts. All other metals except magnesium and the alkalis must, therefore, be removed before the calcium is precipitated; this method is not a separation of calcium except from magnesium and the alkalis.

Procedure. Calcium Weighed as the Carbonate. Weigh out 0.5 g. samples into 400 ml. beakers. Add 20 ml. of water and 5 ml. of concentrated hydrochloric acid, after covering the beaker with a watch glass. Heat the mixture until dissolved (Equation (1)). Rinse down the sides of the beaker and watch glass and dilute to 250 ml. Heat the solution to boiling and add, drop by drop, for each 0.5 g. of sample, a solution of 1 g. of ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, or 0.9 g. of oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, dissolved in about 25 ml. of water. Filter this solution if it is not perfectly clear. These recommended quantities of precipitating agent represent approximately a 50 per cent excess over that theoretically required for pure calcium carbonate. Part of the calcium is usually precipitated in this acid solution. A few drops of methyl red should be present as indicator. To the hot solution add very slowly from a buret a filtered, dilute solution of ammonia—5 ml. of the concentrated reagent to 50 ml. of water—at the rate of about 5 ml. per minute, until the solution is neutral or very slightly alkaline (Equation (2)). Let the solution stand for an hour in a warm place to be assured of complete precipitation. If it is to be left over night, do not keep it warm. (Why?) After the precipitate has settled, test the solution with a few drops of ammonium oxalate for complete precipitation. (Why is it best to avoid a large excess of ammonia?)

Decant the clear supernatant liquid through a filtering crucible; test the filtrate for calcium before discarding it. Transfer the precipitate to the crucible with a jet of water from the wash bottle; rub loose with a rubber-tipped rod all particles adhering to the beaker and stirring rod, and transfer these to the crucible.

Wash the precipitate with cold, very dilute ammonium oxalate—about 0.5 g. of the salt per 200 ml.—at least 10 times, or until the washings give no test for chloride ion. In making this test, add dilute nitric acid to a portion of the washings before adding silver nitrate, in order to prevent any formation of silver oxalate.

Dry the precipitate in the oven for an hour, then place the filtering crucible in the electric muffle, which is maintained at about 500° C., for 2 hours. The crucible may be left in the furnace over night if more convenient. Cool the crucible and contents in a desiccator and weigh. Further heating of the precipitate should not change its weight. Moisten the precipitate with 1 or 2 drops of saturated ammonium carbonate solution, dry at 110° C., and weigh again. A gain in weight is an indication that some oxide was present, which was converted by this treatment into the carbonate. This precaution should *always* be taken.

Calculate the percentage of calcium oxide from the weight of calcium carbonate obtained. The conversion factor is 0.5603.

Procedure. Calcium Weighed as the Oxide. Carry out the precipitation and washing of the calcium oxalate as directed in the preceding method, but filter through an ashless paper filter. Transfer the precipitate and paper to a porcelain or platinum crucible previously ignited and weighed with the cover. Char the filter below a red heat. The crucible need not be covered if heat is applied carefully, and the deposition of tarry matter on the cover is thus avoided. Burn off the carbon as usual, no precaution being necessary to avoid reduction of the precipitate. The oxalate is converted first to the carbonate (Equation (3)); sometimes the carbon monoxide evolved will ignite and burn with a blue flame. After the carbon is burned off, place the covered crucible in a clay cylinder in which a triangle is supported. The cylinder is covered by a clay cover with a hole in the center and is supported on an iron tripod. Heat is supplied by a Meker type of burner which must give a good flame. Only such a burner is satisfactory for this experiment, and the air inlets must be properly opened. Ignite the precipitate at the full heat of the burner for nearly an hour to convert all of the calcium carbonate into calcium oxide (Equation (4)). When partly cool, transfer the crucible to a desiccator and as soon as cool weigh the oxide in the covered crucible. Do not allow the oxide to stand for more than an hour before weighing, or it will absorb carbon dioxide; on the other hand, do not weigh it until cool. Perform the weighing as quickly as possible, for even in a covered crucible calcium oxide will gain in weight while on the balance. Ignite the material again for about 45 minutes and weigh as before, except that this time the proper weights, as previously determined, should already be on the pan and the rider adjusted as accurately as possible, before the crucible is removed from the desiccator, so that the weighing may be made more quickly. Repeat the ignition until successive weights differ by only 0.2 or 0.3 mg. Only in this way may one be certain that the dissociation of the calcium carbonate is complete and that all carbon dioxide has been expelled. If a platinum crucible is available, the necessary temperature is readily obtained with a Meker burner without placing the crucible in the clay cylinder.

Instead of precipitating the calcium by the method just described, ammonia may be added to the hot acid solution until the calcium oxalate just begins to precipitate. The rest of the acid may then be slowly neutralized by keeping the solution, after the addition of 15 g. of urea, just below the boiling point until neutral. This slow neutralization process will require from 20 minutes to 1 hour.[1]

The urea is slowly hydrolyzed:

$$(5)\quad (NH_2)_2CO + H_2O = CO_2 + 2NH_3,$$

and the precipitate obtained in this way is very coarse.

REVIEW QUESTIONS AND PROBLEMS

1. Suggest a method for determining calcium, magnesium, and manganese in a mixture of their carbonates.

2. Write equations for the reactions involved in the determination of zinc and of arsenic in a mixture containing zinc oxide, arsenious oxide and inert substances.

3. The solubility product of strontium oxalate is 5.0×10^{-8}. Calculate the solubility of the salt in a solution 0.01 M in ammonium oxalate.

4. In a 1.0000 g. sample the calcium is precipitated as oxalate, ignited to calcium carbonate and the carbon monoxide formed is oxidized as follows: $5CO + I_2O_5 = 5CO_2 + I_2$. The iodine formed requires for

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[1] F. L. Chan. Dissertation, University of Michigan, 1932.

titration 30.00 ml. of 0.1000 *N* thiosulfate. Calculate the percentage of calcium oxide in the sample.

Ans. 42.06 per cent.

5. The calcium from a 1.0000 g. sample of a limestone is weighed as the carbonate. If 10 mg. of calcium oxide is present in the precipitate that is weighed calculate the error thus introduced in terms of calcium oxide reported.

6. A mixture weighing 0.8820 g. and containing only the anhydrous oxalates of calcium and magnesium loses 0.5402 g. when ignited to oxides. Calculate the percentage of each oxalate.

Ans. 36.31 per cent CaC_2O_4 and 63.69 per cent MgC_2O_4.

7. What volume of sulfuric acid, sp. gr. 1.06, containing 8.77 per cent sulfuric acid by weight, would theoretically be required to convert into calcium sulfate 1.0600 g. of anhydrous calcium oxalate?

8. What weight of ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, would theoretically be required to precipitate the calcium in 1.0690 g. of calcium oxide containing as impurity 2.50 per cent of magnesium as oxide?

9. The solubility product of calcium oxalate is 2×10^{-9} and of lead oxalate 3.4×10^{-11}. In a solution 0.01 *M* in Pb^{++} and Ca^{++} what will be the concentration of Pb^{++} when oxalate is added until calcium oxalate just begins to be precipitated, assuming no change in volume?

10. A solution containing only potassium chloride, potassium sulfate, lithium sulfate, lithium chloride and water was found on analysis to contain 1.1729 g. of potassium, 1.3880 g. of lithium, and 4.803 g. of sulfate ion. What was the weight of chloride ion present?

Ans. 4.6094 g.

DETERMINATION OF IRON IN IRON OXIDE

Principle. The oxide, which may be either Fe_2O_3 or Fe_3O_4, is dissolved in hydrochloric acid since sulfuric acid is very ineffective and nitric acid is almost entirely without action:

$$(1)\quad Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$

$$(2)\quad Fe_3O_4 + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O.$$

Any ferrous salt which is present is oxidized to the ferric form by boiling the solution with a little nitric acid:

$$(3)\quad 3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + NO + 2H_2O.$$

The iron is then precipitated as hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$, by the addition of a slight excess of ammonium hydroxide. A hydrous oxide has no definite stoichiometric composition, but contains a variable amount of water, partly adsorbed and partly bound chemically. It is convenient, however, in writing equations for reactions involving hydrous oxides, and in calculating solubility product constants, to assume the hydroxide formula, although the composition of the precipitate in most cases does not correspond to this formula. The reaction for the precipitation of the hydrous oxide may, for convenience, be written:

$$(4)\quad FeCl_3 + 3NH_4OH = \downarrow Fe(OH)_3 + 3NH_4Cl.$$

The gelatinous precipitate has a tendency to become colloidal, and for this reason it is washed, first by decantation and then on the filter, with a hot 1 per cent solution of ammonium nitrate. The precipitate is ignited at a moderate red heat to ferric oxide in which form it is weighed.

$$(5)\quad 2Fe(OH)_3 \text{ (ignited)} = Fe_2O_3 + 3H_2O$$

or more correctly

$$(6)\quad Fe_2O_3 \cdot xH_2O \text{ (ignited)} = Fe_2O_3 + xH_2O.$$

The presence of a sufficient amount of salts of citric, tartaric, sulfo-salicylic and similar acids, and of glycerine, certain sugars, and alkali pyrophosphate, prevents the precipitation of hydrous oxides when the solution is made alkaline, because of the formation of complex salts. Sulfides, however, such as ferrous sulfide, are precipitated if they can exist in the presence of water; certain separations are, therefore, possible, such as that of iron and manganese from aluminum, chromium, and titanium.

Errors. Hydrous ferric oxide, like all precipitates of a similar character, is, on account of its gelatinous and bulky nature, more difficult to filter and wash thoroughly than any of the precipitates so far encountered. It is colloidal in character and shows a marked tendency to adsorb other sbstances, particularly negative radicals, since it is a positive colloid. Hydrous ferric oxide should be precipitated from a fairly dilute solution and should be washed first by decantation, since by this process the precipitate may be thoroughly stirred up in the wash liquid. When transferred to the filter, hydrous ferric oxide tends to form a compact mass not readily penetrated by the wash water; this is especially true when the precipitate is allowed to remain for a time on the filter, or when suction is used to hasten filtration. In the latter case, the precipitate will appear to be washed more rapidly, but the water runs through little channels and does not permeate the main body of the material. The use of filter paper pulp hastens filtration and facilitates thorough washing. The washing must be continued uninterruptedly after it is once started, and since it is a slow process, plenty of time must be allowed. The precipitate is washed with an electrolyte since it tends to become slimy and colloidal and to clog the filter if water is used. An acid could not be used because it would dissolve the precipitate; a base is inadvisable, because it offers no advantages and tends to take up silica from the glass. The solubility of this precipitate as well as of the other hydrous oxides of this type is negligible, so that no hydroxyl ion is needed. A neutral salt which is volatile on ignition is therefore used; ammonium nitrate is most satisfactory, since it aids somewhat in the subsequent ignition of the precipitate. Ammonium chloride is unsuitable, because during the ignition ferric chloride may be formed which is volatile even below a red heat:

$$(7)\ Fe_2O_3 + 6NH_4Cl = 2FeCl_3 + 6NH_3 + 3H_2O.$$

A similar action does not occur with aluminum oxide. Because of this action between ferric oxide and a chloride, it is desirable to wash out nearly all of the ammonium chloride present in the precipitate, although very small amounts will not react with the oxide.[1] A hot wash solution should be used to make the filtration more rapid.

If all the iron is not present in the ferric form, precipitation will be incomplete, for ferrous hydroxide, like magnesium hydroxide, is only partially precipitated by ammonia.

Any silica in the solution will be largely carried down by the hydrous oxide, and will cause the results to be high. Therefore, fresh, filtered ammonium hydroxide, preferably taken directly from the bottles in which it is shipped, should be added in very slight excess, and the solution should be allowed to stand only a short time before filtering the hydrous ferric oxide. When extreme accuracy is required, freshly distilled ammonia is used and the precipitation is made in platinum vessels. The effect of silica is more noticeable in this precipitation than in any of the others thus far considered, on account of the remarkably adsorptive power of precipitates of this character.

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[1] Daudt, J. Ind. Eng. Chem. 7, 847 (1915).

Ferric oxide is readily reduced during ignition by the organic matter of the filter paper or by the flame gases to Fe_3O_4 or even to metal:

(8) $Fe_2O_3 + 3C = 2Fe + 3CO.$

Such reduction is avoided by burning off the carbon at a low heat, by having at all times free access of air, and by avoiding contact with reducing flame gases.

Other Applications. A number of other metals may be precipitated as hydrous oxides or hydroxides, notably aluminum, chromium (trivalent), and titanium. If an oxidizing agent such as bromine, hydrogen peroxide, or a persulfate is added to the ammoniacal solution, manganese is precipitated as hydrous manganese dioxide. On ignition the oxides formed are: Al_2O_3, Cr_2O_3, TiO_2, Mn_3O_4. Chromium must be entirely in the chromic form before precipitation; any chromate must first be reduced to a chromic salt by some suitable reducing agent such as sulfurous acid, formaldehyde, or alcohol. Permanganate ion must be reduced in a similar manner before the precipitation of manganese.

Since the hydrous oxides of aluminum and chromium are slightly soluble in ammonium hydroxide, care must be taken to avoid adding more than a very slight excess of precipitating agent; in the other cases to which the method is applicable, the precipitate is quite insoluble in ammonia. Complete precipitation occurs in all these cases if the solution is just alkaline to methyl red.[1]

This ammonia precipitation method serves to separate ferric, aluminum, chromium, titanium, and manganic ions from magnesium, calcium, strontium, and barium; a double precipitation is usually necessary, partly because of the adsorption of these latter metals by the precipitate and partly (except with magnesium) because of the absorption of carbon dioxide by the ammoniacal solution, with the formation of ammonium carbonate which precipitates the carbonates of barium, strontium, and calcium. The separation of the hydrous oxides listed above from manganese, zinc, cobalt, nickel, copper, and cadmium is, under usual conditions, not exact enough for quantitative work.

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[1] Blum, J. Am. Chem. Soc. **38**, 1282 (1916).

Even several precipitations fail to remove all the traces of the bivalent metals, and the separation can only be satisfactory when the precipitate of hydrous oxide is so small that the amount of other metals adsorbed is slight enough to be disregarded. Iron, titanium, and, less satisfactorily, aluminum, but not chromium, are separated from the zinc and calcium groups but not from the acid hydrogen sulfide group by the "Basic Acetate Method."

The concentration of hydrogen ion at which the various metals are precipitated as hydroxides or basic salts is of great importance, because it shows what separations are likely to be feasible and it gives the relative strengths of the bases. (See Table XVIII, p. 378.) In most cases the precipitate is, initially, a basic salt rather than a true hydroxide or hydrous oxide.

An efficient separation of the very weak bases from the stronger ones can be made only by taking account of several conditions:

1. *Careful control of* pH. This may be regulated by means of a buffer mixture as in the basic acetate or benzoate methods, by choosing a weak base of suitable strength as in the ammonia method, or by using some internal reaction which will slowly increase the *p*H of the solution to the proper value. An example of the last case is the hydrolysis of urea to form ammonia and carbon dioxide, a reaction already described under the determination of calcium.

2. *Homogeneity of the solution.* When a drop of ammonia is added, there is a high concentration of hydroxyl ion where the drop mixes with the solution, and other hydroxides in addition to the one desired may precipitate. As the mixing becomes complete, these other hydroxides may not entirely dissolve. Such a condition is avoided in the basic acetate, benzoate and urea methods, especially in the latter, because in these cases the reagents are added before precipitation begins and the precipitation is brought about by an internal reaction which results from heating the solution. The *p*H of the solution is, therefore, uniform throughout.

3. *Slow precipitation.* This is very satisfactorily accomplished by the urea or similar methods.

4. *A suitable anion which can form a dense precipitate of basic salt.* This procedure allows complete precipitation at a lower *p*H than would be possible in forming the hydrous oxide. If

the anion is suitably chosen the precipitate is denser and therefore less adsorption occurs. The basic acetate method has already been mentioned. It does not give a dense precipitate. Benzoate ion is better,[1] but the best results are obtained by the method of Willard and Tang.[2] These authors used urea to precipitate aluminum as the dense basic succinate and obtained remarkably sharp separations of aluminum even from large amounts of zinc, cobalt, nickel, and other metals from which aluminum cannot be completely separated by ammonia or even by the basic acetate or benzoate methods. Succinate does not, however, give a dense precipitate with ferric iron but formate does and sulfate is effective with both.

Interfering Substances. It is evident from the statements already made that in precipitating a metal by the ammonium hydroxide method, all other metals similarly precipitated must be absent; likewise, even those metals soluble in excess of ammonia, since they will contaminate the precipitate. Such acids as phosphoric, arsenic, oxalic, citric, and tartaric, which either form insoluble ferric salts or, by complex formation, prevent the precipitation of the hydrous oxide, and also silicic acid, must be absent. Only calcium, strontium, barium, magnesium, and the alkali metals may be present. Under carefully regulated conditions a separation from nickel and from manganese is also possible.[3]

Procedure. Weigh out 0.5 g. samples (if much larger, the precipitate will be inconveniently bulky) into 150 ml. beakers, and add 10 ml. of water and 20 ml. of concentrated hydrochloric acid. Cover the beaker and heat the material just below the boiling point until the sample is dissolved. The time required, usually ½ hour to 1 hour, will depend upon the temperature, as the action in the cold is extremely slow. Do not allow the solution to evaporate to less than 5 or 10 ml.; add more acid if necessary. To determine whether all iron oxide is dissolved, give the solution a rotary motion which will cause any undissolved particles to collect in the center. Continue the application of heat until no dark particles remain. (Equations (1) and (2)). Add

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[1] Kolthoff, Stenger and Moskovitz, J. Am. Chem. Soc. **56**, 812 (1934).

[2] Willard and Tang, J. Am. Chem. Soc. **59**, 1190 (1937); Ind. Eng. Chem. Anal. Ed. **9**, 357 (1937).

[3] Lundell and Knowles, J. Am. Chem. Soc. **45**, 676 (1923).

1 ml. of concentrated nitric acid to the solution, and boil a moment to oxidize any ferrous chloride (Equation (3)). A slight white residue of silica is usually present, but even if no residue can be seen, dilute the solution somewhat, filter through a small filter into a 600 ml. beaker, and wash the filter thoroughly with dilute hydrochloric acid—1 ml. of concentrated acid to 100 ml. of water—to prevent hydrolysis of the ferric chloride. Dilute the filtrate to 300 ml. Never use a filtering crucible: it will quickly become clogged.

The filtration and washing of gelatinous precipitates is hastened by the use of ashless filter paper pulp. This is most conveniently prepared by tearing up about one-fourth of a filter pulp tablet, and shaking the pieces vigorously for a moment in a test tube with a little water. This amount of pulp is sufficient for one sample, and should be added to the clear ferric chloride solution.

Do not start the precipitation unless a period of at least two and a half hours is available. Heat the solution to boiling and add filtered, concentrated ammonium hydroxide slowly, with constant stirring, until the precipitate of ferric hydroxide coagulates and the steam has a slight odor of ammonia (Equation (4)). Avoid a large excess of the ammonia. (Why?) Boil the solution gently for a minute; then let it settle. The supernatant liquid should be colorless. The precipitation of hydrous ferric oxide is complete at once. As soon as most of the precipitate has settled, decant the hot supernatant liquid through a loosely textured filter, but leave as much of the precipitate as possible in the beaker. It is essential that the filter paper fit the funnel properly, so that the stem of the funnel is filled with liquid. Otherwise filtration will be very slow.

In the meantime, make up enough wash solution to fill two 800 ml. beakers—1 g. of ammonium nitrate to 100 ml. of water with 1 drop of ammonia in each beaker—and have it at the boiling point. Add about 100 ml. of this hot solution to the precipitate, stir the mixture thoroughly and let the precipitate settle. Decant as much liquid as possible through the filter. Repeat this method of washing by decantation several times, in order to remove most of the salts from the precipitate. Transfer the precipitate to the filter; rub loose with a rubber-tipped rod all particles adhering to the beaker and stirring rod and transfer these to the main bulk of precipitate. Wash the hydrous ferric oxide, at least 5 or 6 times, with hot ammonium nitrate solution until no test, or only a very slight test, for chloride ion is obtained from the washings. Let each portion of wash liquid run through before adding the next portion. Do not fill the filter more than three-fourths full of precipitate; if necessary, use a second filter instead of one large one. Take care not to get the different samples mixed. Traces of precipitate which may adhere to the sides of the beaker may often be wiped off with a piece of moist filter paper which is then added to the main precipitate after the latter is washed, or the adhering oxide may be dissolved by a few drops of concentrated nitric acid, and be reprecipitated by ammonia. Fold over the edge of the filter and transfer the precipitate and filter to a porcelain crucible previously ignited and weighed without the cover. Dry the material over a low flame, and char the paper below a red heat. Burn off the carbon at a low temperature, and take particular care to avoid reduction of the oxide (Equation (8)). Raise the temperature to a red heat to dehydrate the hydrous oxide (Equations (5) and (6)); keep the flame on the bottom of the crucible and do not allow gases to get inside the crucible (see p. 32). Ignite the precipitate for 30 minutes after the filter is burned; then cool and weigh as ferric oxide. Repeat the ignition until the weight of the material is constant. The oxide may have a lustrous black appearance like that of magnetic oxide, Fe_3O_4, but such an effect is usually due to the compactness of the solid and is only superficial, as can easily be seen by crushing some of the material after the final weight has been taken. The presence of any iron or magnetic oxide will make the precipitate magnetic.

Calculate the percentage of iron from the weight of ferric oxide thus obtained. The factor for converting ferric oxide into iron is 0.6994.

Basic Acetate Separation. The principle involved in this method is discussed on p. 379. It is a standard method for separating the very weak bases, ferric iron and titanium (and phosphate ion unless excess of it is present) from manganese, zinc, cobalt, and nickel, and less frequently from calcium, barium, strontium, and magnesium. A simple ammonia precipitation, which is more easily accomplished, is effective with the last four but not with the others. Chromium is only partially precipitated because it forms with acetate ion a fairly stable complex ion. Aluminum is likely to be incompletely precipitated. Metals of the acid hydrogen sulfide group must first be removed. Chloride solutions give the most satisfactory results.

The hydrolysis of ferric chloride does not go to completion because of the accumulation of hydrogen ion. If an ion such as the acetate ion is introduced, which is capable of forming a weak acid with the hydrogen ion, the hydrolysis is much more extensive. The mixture of an acetate and acetic acid acts as a buffer to prevent the concentration of hydrogen ion from becoming too great. The solution is heated to promote hydrolysis and the precipitate is a basic acetate of indefinite composition, which is converted into ferric oxide upon ignition. In the separation of iron and manganese, it is very important to have a solution of the right acidity before the sodium acetate is added. Brunck's[1] method for removing excess of hydrochloric acid is a simple and excellent one. The procedure is as follows: Add about 1 g. of potassium chloride to the acid solution of the metallic chlorides and evaporate to apparent dryness. Break up the residue and heat it at 100° C. until the odor of hydrochloric acid is faint (5-7 minutes). In the presence of potassium chloride, it is possible to carry the evaporation to dryness without decomposition of ferric chloride. Enough hydrochloric acid remains to give a clear solution when the residue is treated with 20 ml. of water. Dissolve 3 g. of sodium acetate in 100 ml. of water and make this solution neutral to litmus by the addition of 1 per cent acetic acid. Add the sodium acetate solution to the ferric chloride solution, dilute to 300-500 ml., heat just to boiling and hold at this temperature for 1 minute. The basic acetate soon precipitates. Filter the material while hot and wash the precipitate with hot, 1 per cent ammonium acetate solution. Before precipitation the *p*H of the cold solution should be between 4.7 and 5.3; if it is less than 4.3, the iron is not completely precipitated. Any phosphate ion present is precipitated as ferric phosphate. If too much acetate ion is added, the concentration of hydrogen ion may be sufficiently reduced to allow hydrous manganic oxide or manganese dioxide to precipitate. The oxygen of the air acts as the oxidizing agent.

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[1] Brunck, Chem. Ztg. **28**, 514 (1908).

The benzoate method[1] gives a precipitate which is much more easily filtered, especially that formed with ferric and chromic ions. To the acid solution containing at least 1 g. of ammonium chloride add dilute ammonium hydroxide until the precipitate first formed dissolves very slowly upon stirring. Add 1 ml. of glacial acetic acid and 20 ml. of 10 per cent ammonium benzoate solution for every 65 mg. of aluminum or 125 mg. of iron present. Boil gently 5 minutes, filter and wash with hot 1 per cent ammonium benzoate containing 2 per cent of acetic acid.

REVIEW QUESTIONS AND PROBLEMS

1. Why must all ferrous iron be converted to the ferric state before the precipitation of total iron by ammonium hydroxide is made? What other ions does ferrous ion resemble in its behavior toward ammonium hydroxide in the presence of ammonium chloride?

2. What substances will prevent the precipitation of hydrous oxides by excess of ammonium hydroxide? In what way do these organic compounds resemble each other?

3. Explain why the precipitation of hydrous oxides by ammonium hydroxide gives a less complete separation from nickel, zinc, manganese, etc., than the basic acetate or benzoate method and why the urea method is still more effective.

4. In general what data would indicate the possibility of separating two metals by precipitating one of them as hydrous oxide? How can the adsorption of foreign cations be reduced?

5. Classify the following metals, in order, according to their strength as bases: aluminum, titanium, ferric iron, ferrous iron, zinc, chromium, calcium, magnesium. Which of these are amphoteric?

6. Why is the volumetric determination of iron more accurate and convenient than the gravimetric? What would be the best method of finding the weight of each oxide in a mixture containing ferric oxide and aluminum oxide in approximately equal amounts?

7. One g. of ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, is heated to 1000° C. What is the weight of the residue?

8. The ignited precipitate of ferric oxide and aluminum oxide from a sample weighing 1.0230 g. weighs 0.4550 g. When it is ignited in hydrogen the ferric oxide is reduced to metallic iron, and the loss in weight is 0.120 g. Calculate the percentage of each oxide in the sample.
Ans. 39.03 per cent Fe_2O_3 and 5.45 per cent Al_2O_3.

9. A sample of ferric oxide loses 0.1200 g. when ignited in hydrogen. It is dissolved in dilute sulfuric acid out of contact with air and titrated with 0.1000 *N* permanganate. How many ml. would be required?

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[1] Kolthoff, Stenger and Moskovitz, J. Am. Chem. Soc. **56**, 812 (1934).

10. The precipitate of ferric oxide from a 1.000 g. sample weighed 0.3094 g. It contained a little magnetic oxide, Fe_3O_4. It was reduced in hydrogen to iron, which weighed 0.2234 g. Calculate the error in per cent of ferric oxide caused by assuming that the precipitate was pure ferric oxide.

Ans. 1.00 per cent low.

11. One g. of a mixture containing only ferrous oxide and metallic iron when dissolved in dilute sulfuric acid yields 100.0 ml. of hydrogen at 740 mm. and 20° C. Calculate the composition of the mixture. (One liter of hydrogen under standard conditions weighs 0.08987 g.).

12. Outline a suitable procedure for the determination of iron, magnesium and calcium in a mixture of their oxides and carbonates.

13. One g. of pure ferrous carbonate is ignited in the air to ferric oxide. What is the weight of the residue?

14. Ten g. of iron is dissolved in excess of dilute sulfuric acid and the ferrous sulfate thus formed is oxidized to ferric sulfate by the addition of 3 per cent hydrogen peroxide (density 1.010). How many ml. will be required? Suggestion: Write the equations but do not calculate the weight of ferrous sulfate.

15. Ten g. of magnetic oxide, Fe_3O_4, treated as in problem 14 would require how many ml. of 3 per cent hydrogen peroxide?

16. In the determination of magnesium the precipitate of magnesium pyrophosphate is contaminated by the unsuspected presence of manganese pyrophosphate from 1.10 per cent of manganese in the sample. What error does this cause in the per cent of magnesium?

17. In problem 16 what error would be caused by the presence of 1.50 per cent of iron present as ferric phosphate, $FePO_4$? Ans. 0.885 per cent.

18. Ten g. of metallic chromium, dissolved in hydrochloric acid to form chromous chloride, $CrCl_2$, will absorb what volume of oxygen under standard conditions, in forming chromic chloride, $CrCl_3$, if 1 liter of oxygen weighs 1.4289 g.?

DETERMINATION OF SILICA IN A SOLUBLE (BASIC) SILICATE

Principle. Silicic acid, one of the weakest acids known and consisting of silicon dioxide combined with varying proportions of water, has no definite formula. Its composition may be expressed as $SiO_2 \cdot xH_2O$, although it is often convenient in writing equations to assume some simple formula, as H_2SiO_3. As might be expected, therefore, there is a very large variety of naturally occurring and artificial silicates, many of which have a definite formula, and many of which do not. All silicates may be considered as compounds of silicon dioxide with different oxides, and their formulas are often written in this way, for example $2CaO \cdot SiO_2$ instead of Ca_2SiO_4.

For analytical purposes, silicates may be divided into two classes: those which dissolve in an acid such as hydrochloric acid to form hydrated silica and chlorides of the metals present, and those which are insoluble in any acid except hydrofluoric acid. Among the soluble silicates are Portland cement and blast furnace slag. There are also many silicates which are partially soluble. The soluble silicates are strongly basic, that is, they contain a relatively large proportion of strong or fairly strong basic constituents, such as oxides of calcium, barium, strontium, zinc, lead, or the alkalis. It is, for example, possible to have two calcium silicates, one soluble, containing a relatively high ratio of calcium oxide to silica, and the other insoluble in acids. To render one of the latter type decomposable for analysis, it must be converted into the soluble, more basic form by supplying the necessary excess of a strong base. This is done by igniting or fusing it with some strongly basic reagent such as the hydroxide, oxide, or carbonate of the alkalis or alkaline earths. Sodium carbonate is the reagent most commonly used because it is fusible and it avoids the introduction of interfering metals: a platinum crucible is required (why?). If alkali hydroxides are used, a nickel crucible is preferred, since platinum is badly attacked. After this treatment the basic silicate is readily decomposed by hydrochloric acid, forming hydrated silica, commonly called silicic acid, and chlorides of the metals.

The treatment with hydrochloric acid often results in a clear solution containing silica in a highly dispersed form. As the solution stands, especially if it is hot, the particles of silica aggregate to form a precipitate or gel:

$$(1)\quad Ca_2SiO_4 + 4HCl = 2CaCl_2 + SiO_2 + 2H_2O.$$

Much of the silica, however, remains in colloidal solution and for a complete separation it is necessary to evaporate the solution to dryness and thus dehydrate the silica. All the water is not lost below a red heat; after dehydration at 105°-120° C. the silica still contains 5 or 10 per cent of water. It has, however, by the aggregation of the particles, largely lost its property of becoming dispersed, especially in the presence of an acid, the hydrogen ion of which tends to coagulate or prevent dispersion of the negative colloid, silica.

Hot, concentrated sulfuric acid and also perchloric acid[1] are very effective dehydrating agents and are often used, especially the latter. A dehydration with perchloric acid can be completed much more quickly than an evaporation to dryness and a purer silica precipitate is obtained. Furthermore, the perchlorates are all soluble.

The dry mass containing basic chlorides and oxides, if salts of very weak bases are present, is treated with hydrochloric acid and the soluble chlorides are dissolved. The silica which is left is filtered off and ignited at a very high temperature to complete the dehydration and to convert the precipitate into anhydrous silicon dioxide, in which form it is weighed. A little silica always remains in solution and can be recovered only by a second evaporation after the main portion has been filtered off. The amount remaining in solution is greater, the larger the amount originally present. With a high percentage of silica it may be as much as 10 mg., although with care it may be made much less. If the amount of silica in the sample is very small, one dehydration is evidently sufficient. Two dehydrations without intervening filtration will remove but little more silica than one dehydration. Most of the silica must be actually removed before the little that remains can be recovered. Even two evaporations will not remove every trace of silica, but more dehydrations would accomplish nothing. The silica which remains will be largely carried down by any subsequent precipitation of hydrous aluminum or ferric oxide. This subject is thoroughly discussed by Hillebrand.[2] Lenher and Merrill[3] found that gelatinous silica attains its maximum dispersion in water at 25° C. after a period of 8 days, and that at the end of this period a colloidal solution containing 16 mg. of silica per 100 ml. of solution resulted. At 90° C., after a period of 24 hours, such a solution contained 43 mg. of silica. For a 10 per cent hydrochloric acid

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[1] Willard and Cake, J. Am. Chem. Soc. **42**, 2208 (1920); Meier and Fleischmann, Z. anal. Chem. **88**, 84 (1932).

[2] Hillebrand, J. Am. Chem. Soc. **24**, 362 (1902).

[3] Lenher and Merrill, J. Am. Chem. Soc. **39**, 2630 (1917).

solution instead of water, the corresponding figures are 6 mg. and 18 mg. By long grinding of silica in water, colloidal solutions are easily obtained. Therefore, the rapidity of dispersion is greater the more hydrated the silica and the greater the surface of it exposed. These facts indicate why two recoveries of silica are required when a considerable amount of it is present. It is evident also that an accurate determination of silica is possible only because dehydrated silica is so slowly dispersed by dilute acids. It should be noted that this is a matter of the rate of dipersion and not of true solubility.

The precipitate of silicon dioxide is washed with dilute hydrochloric acid if salts of weak bases are present, such as ferric and aluminum chlorides, to prevent hydrolysis of these materials and consequent contamination of the precipitate with ferric oxide, etc. The hydrochloric acid is then washed out with water, for otherwise it is difficult to burn off all the carbon during ignition. If only alkali salts are present, the precipitate is washed with water. Silicon dioxide is not reduced by the carbon. Most of the silica not previously separated may be recovered from the precipitate of hydrous ferric and aluminum oxides.

The silica thus obtained is never perfectly pure but always contains small amounts of the oxides of the very weak bases present in the substance, such as aluminum oxide, ferric oxide, or titanium oxide, resulting from the hydrolysis of the chlorides. Practically none of the oxides of the stronger bases are in the precipitate because the chlorides of these metals are only slightly hydrolyzed during the dehydration process. Aluminum oxide and titanium oxide, especially the latter, are less soluble in acids than ferric oxide, and therefore are present in relatively larger amounts in the precipitate. In precise work, this impurity must be determined as follows: The weighed precipitate is treated in a platinum crucible with an excess of hydrofluoric acid and a small amount of sulfuric acid, the latter acid being used to expel all fluoride ion on evaporation. The first action of hydrofluoric acid on silicon dioxide is the formation of hydrofluosilicic acid, H_2SiF_6, which, on evaporation of the solution, breaks up into hydrofluoric acid and silicon tetrafluoride. Since the latter is a gas, all of the silicon dioxide is removed and only the sulfates remain. The final reactions may be expressed as follows, by using aluminum oxide as an example of an impurity:

(2) $SiO_2 + 6HF = H_2SiF_6 + 2H_2O$.
(3) H_2SiF_6 (+ heat) = $SiF_4 + 2HF$.
(4) $Al_2O_3 + 6HF = 2AlF_3 + 3H_2O$.
(5) $2AlF_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6HF$

The impurities were weighed as oxides in the original precipitate, and therefore must finally be weighed again as oxides after the silica has been volatilized. If no sulfuric acid were added, they would be weighed as fluorides. Evaporation with sulfuric acid expels all hydrofluoric acid, owing to the difference in boiling points of these acids. The residue of sulfates is then ignited to oxides and weighed as such:

(6) $Al_2(SO_4)_3$ (ignited) = $Al_2O_3 + 3SO_3$.

The total loss in weight is evidently due only to loss of silicon dioxide, provided that the residue consists of oxides, and this is true if it is small and if only very weak bases are present. If the residue is large, or if stronger bases are present, it is impossible to drive off all of the sulfur trioxide from the precipitate and the results for silica will be low.

This same reaction may be utilized to decompose silicates for analysis, when it is not desired to determine the silica but simply to remove it. The metals are obtained in the form of soluble sulfates. The method is, however, rather troublesome and requires the use of platinum vessels.

The separation of silica must obviously precede all other separations, since, if this order is not followed, all the precipitates subsequently formed are likely to be contaminated with silica.

Errors. The amount of silica remaining in solution is greater, the less complete the dehydration has been. Too low a temperature during this process will, therefore, cause low results. Too high a temperature, on the other hand, is likewise injurious, for the silica, although completely separated, carries with it a considerable amount of iron, aluminum, magnesium, etc., in the form of insoluble compounds, and is thus much less pure. A temperature of 100°-120° C. for dehydration is most satisfactory.

The silica is never absolutely pure, no matter how carefully it is separated, but the amount of impurity should be kept as low as possible. The total impurity may be determined as described on pp. 358, 408.

Some silica may be taken up from the glass or porcelain vessels used.

Care is required in the ignition of the silica. The precipitate is so very light that a slight air current is sufficient to carry away a little of the powder, and the draft from the burner may do this.

Procedure. Samples suitable for this work are all soluble basic silicates, such as blast furnace slag, Portland cement, and basic calcium aluminum silicate containing varying quantities of other elements. Weigh out 1 g. samples into 150 ml. beakers, add 50 ml. of water, and stir the sample thoroughly to avoid hardening of the cement. Cover, boil the mixture for a minute or two to disintegrate the powder thoroughly, allow it to cool somewhat and add rapidly with constant stirring 25 ml. of concentrated hydrochloric acid. Keep the mixture hot to avoid the separation of much silicic acid, but do not boil it. Stir frequently. After a few minutes all the powder should dissolve except perhaps a few hard grains of insoluble matter. (Equation (1), p. 356.) As the solution stands, gelatinous silicic acid usually separates. Rinse off the stirring rod and the cover, hang three glass hooks over the edge of the beaker to facilitate evaporation, put a watch glass on these hooks, thus lifting it from the edge of the beaker, and place the beaker on a low temperature hot plate to evaporate the solution to dryness.

Great care must be taken to avoid spattering, which is certain to occur if the gelatinous mass becomes too hot. This dehydration should be conducted on a low temperature hot plate where the temperature will not be above 120° C. (Why?) The residue must be thoroughly dry. (Why?) During the evaporation the chlorides of iron and aluminum form basic salts, such as $Al_2O_3 \cdot AlCl_3$, insoluble in water and dilute hydrochloric acid, but largely soluble in concentrated hydrochloric acid. The dry residue should be left on the hot plate for at least 1 hour, though longer heating at this temperature, as overnight, is not harmful. Cool, add 5 ml. of concentrated hydrochloric acid, and warm the mixture gently to dissolve the basic salts. The time required may vary from 5 to 30 minutes, and will depend on the temperature and duration of the dehydration. It is essential that the concentrated acid should act until all basic salts have dissolved. Otherwise, these salts will remain insoluble when the acid solution is diluted. Add 20 ml. of water and rub the precipitate loose with a rubber-tipped rod. Evaporate the solution again and dehydrate as before. During the second evaporation the silica is in a granular instead of gelatinous form, and encloses less impurity; it is also much more slowly soluble in acid. Treat the residue as before with 5 ml. of concentrated hydrochloric acid, and heat the material until basic salts are dissolved. Dilute the solution with 25 ml. of water, and heat for 10 or 15 minutes, or until everything but the silica is dissolved. Rub the precipitate loose, filter and wash it 10 times with dilute hydrochloric acid—1 ml. of the concentrated acid to 100 ml. of water—then with water until the washings are free from acid. (Why wash first with acid, and then with water?) Fold up the damp filter, and set it aside until the second recovery of silica is completed.

A little silica always remains in the filtrate. Evaporate the filtrate and washings to dryness and dehydrate as before. Treat the residue with concentrated hydrochloric acid, then add water, etc. Filter the solution through a separate filter. (Why?) The action of the hydrochloric acid, both before and after dilution, should not be excessively prolonged, for otherwise some of the silica becomes dispersed; sufficient time must be given to dissolve out all salts. Without drying, transfer both precipitates to a porcelain crucible previously ignited and weighed without the cover. Char the paper, then burn off the carbon over a low flame as usual. Take care that none of the fine powder is blown away. When the precipitate is white, cover the crucible, placed preferably on a triangle inside a clay cylinder to increase the temperature, and heat it for one hour at the full temperature of the Meker burner to complete the dehydration. Weigh the silica and repeat these ignitions until the weight is constant. If the precipitate is slightly pink due to the presence of ferric oxide, the temperature of dehydration was too high or the concentrated hydrochloric acid did not act long enough to dissolve the basic salts. This error can usually be noticed while the precipitate is being washed. In such a case the sample should be discarded at once and a new one started, for it is practically impossible to dissolve out this impurity. If the precipitate is gray, carelessness in burning off the carbon or failure to wash the hydrochloric acid out of the filter paper is indicated.

The silica thus obtained, as stated before, is not perfectly pure. It may, however, be reported as impure silica if the platinum crucibles required to determine the amount of impurity are not provided. (How would this be done?) Calculate the percentage of silica.

If an insoluble silicate is to be analyzed, it is first fused with 6 to 8 times its weight of anhydrous sodium carbonate in a platinum crucible until the fusion is quiet. After cooling, the crucible is placed in dilute hydrochloric acid until the contents can be completely removed; the crucible is then rinsed off, removed, and the solution treated as above.

If it is desired to use perchloric acid as a dehydrating agent the sample is stirred up with 10 ml. of water, after which 2 ml. of concentrated hydrochloric acid and 15 ml. of 60-70 per cent perchloric acid are added. The solution is evaporated on the hot plate until dense white fumes of perchloric acid appear, and then boiled *gently* 15 minutes with the beaker covered to prevent much loss of acid. The solution is cooled somewhat and 70 ml. of dilute hydrochloric acid added (one part of acid to nine of water). It is heated nearly to boiling, filtered and washed as directed in the preceding method.[1] There is less impurity in silica obtained in this way because the concentrated acid prevents the formation of basic salts.

REVIEW QUESTIONS AND PROBLEMS

1. Give each step in the complete analysis of an insoluble complex silicate of manganese, magnesium and iron.

2. Outline a method for the determination of cadmium, calcium, and magnesium in a soluble silicate.

3. With what oxides is a precipitate of silica most likely to be contaminated? Why? If the silica is determined by the loss when it is volatilized, why are the results low when the amount of impurity is considerable?

4. What volume of hydrofluoric acid, sp. gr. 1.15 and containing 48 per cent of HF, is theoretically required to volatilize 1.5 g. of pure silica?

5. A sample of pure anhydrous sodium silicate weighing 1.0000 g. is evaporated with an excess of hydrofluoric and sulfuric acids and the residue, which has been heated to drive off all free acid, weighs 0.6500 g. What per cent of silica in the sample?
Ans. 71.63 per cent.

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[1] Do not dry the paper in an oven. A slight amount of perchloric acid remaining may be enough to cause a sufficient explosion to damage glass vessels in the oven. See p. 22.

6. Would you expect a silicate containing only silica and alumina in any proportion to be soluble? Explain.

7. A silicate contains 16.92 per cent K_2O, 18.32 per cent Al_2O_3 and 64.76 per cent SiO_2. What is its formula?

8. One g. of manganous silicate is evaporated with hydrofluoric and sulfuric acids and the residue ignited to Mn_3O_4, which weighed 0.5200 g. What per cent of silica in the sample, assuming that no other elements are present?

Ans. 51.64 per cent.

9. A sample of cyanide contains 60.00 per cent potassium cyanide and 40.00 per cent sodium cyanide. If the per cent of cyanogen is determined and calculated as potassium cyanide what percentage of the latter is apparently present? If calculated as sodium cyanide?

10. A sample of clay contains 12.00 per cent moisture and 70.00 per cent silica. What would be the percentage of silica calculated on a dry basis?

DETERMINATION OF SULFUR IN A SULFIDE

Principle. The sulfides that occur most commonly are those of lead, arsenic, copper, nickel, zinc, and iron, the last occurring usually as "iron pyrites," FeS_2. Three methods are commonly available for the gravimetric determination of sulfur in such compounds. In two of them the sulfide is oxidized directly to the sulfate; in the third it is first converted into hydrogen sulfide, which is then oxidized to the sulfate.

Method 1. Oxidation by fusion with an alkaline oxidizing agent such as sodium peroxide, or, less efficiently, sodium carbonate with potassium nitrate or potassium chlorate.

$$(1)\quad 2FeS_2 + 15Na_2O_2 = \downarrow Fe_2O_3 + 4Na_2SO_4 + 11Na_2O.$$

$$(2)\quad 3ZnS + 2Na_2CO_3 + 8NaNO_3 = 3Na_2ZnO_2 + 3Na_2SO_4 + 8NO + 2CO_2.$$

The sulfide is always fused in an iron or nickel crucible if peroxide is used, since these metals, especially nickel, are less attacked than is platinum. The alkaline solution obtained from treatment of the fused mass with water is filtered and acidified. After removal of the excess of peroxide by boiling, the sulfate ion is precipitated with barium chloride as usual.

$$(3)\quad Na_2ZnO_2 + Na_2SO_4 + 4HCl = 2NaCl + Na_2SO_4 + ZnCl_2 + 2H_2O.$$

$$(4)\quad Na_2SO_4 + BaCl_2 = \downarrow BaSO_4 + 2NaCl.$$

Since these oxidizing agents, especially sodium peroxide, are very powerful, they will readily oxidize all sulfides. Other advantages in their use are their rapidity of action and the removal from the alkaline solution by filtration of all metals except those forming soluble salts with sodium hydroxide, such as sodium aluminate, $NaAlO_2$, sodium plumbate, Na_2PbO_3, etc. This method has, however, certain disadvantages: fused sodium peroxide attacks the crucible to some extent, and appreciable amounts of sodium salts are introduced, producing the errors described in connection with the determination of sulfate ion. Some metals are not removed, but these usually do no harm. The use of a carbonate-nitrate mixture makes necessary an evaporation with hydrochloric acid to remove nitrate ion. (Why?)

Method 2. Oxidation by an oxidizing solution such as bromine followed by nitric acid; sodium chlorate and nitric acid; hydrochloric acid and bromine; nitric and hydrochloric acids. A solution of bromine in carbon tetrachloride or chloroform is often used and followed by nitric acid.

$$(5)\quad FeS + 9Br + 3HCl + 4H_2O = FeCl_3 + H_2SO_4 + 9HBr.$$

$$(6)\quad FeS + 3HNO_3 + 3HCl = FeCl_3 + H_2SO_4 + 3NO + 2H_2O.$$

This method has the advantage of not introducing any metallic ions, but the excess of nitric acid must be removed. (How?) It has the disadvantage of not removing any metals. Also the oxidizing agents used are not so powerful as the fusion mixture and their action is therefore slower and not as certain unless exceptional care is taken. The method is an excellent one when the metals present do not interfere, as for the analysis of the sulfides of zinc, copper, and nickel. If interfering metals such as ferric iron are present, they must be removed, or the ferric ion may be reduced to the less interfering ferrous ion (by zinc or aluminum, for example).

Method 3. Conversion into hydrogen sulfide, which is absorbed in a suitable apparatus. Some sulfides, such as zinc sulfide and ferrous sulfide, are soluble in hydrochloric acid with evolution of all the sulfur as hydrogen sulfide:

$$(7)\quad FeS + 2HCl = FeCl_2 + H_2S.$$

Others, such as copper sulfide, iron pyrites, mercuric sulfide, etc., are not completely decomposed by hydrochloric acid. All sulfides may, however, be rendered soluble by heating them with powdered iron; this procedure should never be used in any other method, because it would be unnecessary and would introduce a large amount of iron with the consequent disadvantages mentioned above.

(8) $CuS + Fe = Cu + FeS$.

(9) $Cu + FeS + 2HCl = Cu + FeCl_2 + H_2S$.

The hydrogen sulfide formed is passed into an ammoniacal solution of hydrogen peroxide and is thus oxidized to sulfate ion. Unless hydrogen peroxide is present in the ammonia, loss of sulfur will occur due to the volatility of the ammonium sulfide. Also, the solution must be alkaline or free sulfur will be formed by the action of the hydrogen sulfide with the hydrogen peroxide.

(10) $H_2S + 2NH_4OH + 4H_2O_2 = (NH_4)_2SO_4 + 6H_2O$.

The excess of ammonia is boiled off, all peroxide being destroyed in the same process, and the sulfate ion is precipitated as barium sulfate in the usual way. Since no interfering substances are present, this method is capable of great accuracy. Sodium peroxide could be used instead of ammonia and hydrogen peroxide. The hydrogen sulfide, if small in amount, may also be determined volumetrically, in which fact lies one great value of the method. It is especially important in the determination of sulfur in iron and steel in which the sulfur exists as sulfide. This reaction has already been discussed, pp. 278-279.

If any sulfate is present with the sulfide, methods 1 and 2 will obviously indicate only the total amount of sulfur present and will not distinguish between the two forms, since all of the sulfur is finally converted into the one form before precipitation. In method 3, however, all the hydrogen sulfide evolved comes from the sulfide, the sulfate remaining unchanged, provided that the original sulfide is treated with hydrochloric acid. If the sulfide has first been ignited with iron to render it soluble in hydrochloric acid, the sulfate is reduced to sulfide:

(11) $FeSO_4 + 3Fe = FeS + Fe_3O_4$

and the hydrogen sulfide evolved represents the sulfur from both sources.

If it is desired to determine only sulfide sulfur in an insoluble sulfide mixed with sulfate, the former may be converted into hydrogen sulfide by boiling the mixture with metallic tin and rather concentrated hydrochloric acid, the nascent hydrogen acting on the sulfide.

Some sulfides may be determined by burning them in oxygen:

$$(12)\quad 2FeS_2 + 11O = Fe_2O_3 + 4SO_2$$

and passing the sulfur dioxide evolved into an oxidizing solution to convert it into a sulfate, or volumetrically by absorbing it in standard sodium hydroxide containing hydrogen peroxide and titrating back the excess of alkali. This is applicable to iron and steel.

The sodium peroxide fusion method is preferred on account of its simplicity. The sulfides analyzed are mostly cupric, cuprous, nickel, zinc, and cadmium sulfides, and iron pyrites. *When both the metal and sulfur* in a sulfide are to be determined, two samples are always used. The one in which the metal is to be determined is never fused since such a process would cause the introduction of impurities from the crucible. This sample is always dissolved in nitric acid or in nitric and hydrochloric acids, since all sulfides are soluble in these acids. Sometimes hydrochloric acid may be used.

Errors of the Peroxide Fusion Method. If the crucible is heated by city gas which always contains sulfur, the sulfur dioxide formed by combustion will be absorbed in varying quantities by the fused peroxide and this error will be greater the longer the heating process. The error may be avoided by using gas free from sulfur, such as butane, or by electric heating, and when city gas is used, the error may be reduced to a negligible quantity by fitting the crucible into a hole in a sheet of asbestos to deflect the products of combustion and by keeping the crucible covered during the ignition. A small flame should be used with the crucible near the top of the burner. A large flame causes the formation of more sulfur dioxide.

The precipitate of oxides, which is filtered off, retains sulfate ion very tenaciously and must be very thoroughly washed to avoid low results. The crucible is appreciably attacked, especially at higher temperatures, and thus the bulk of this precipitate is increased. The action on the crucible may be decreased somewhat by lining it with sodium carbonate. About 6-7 g. of the dry salt is fused in the crucible. While this liquid flux is cooling, the crucible is rotated to spread the salt uniformly over the sides and bottom. The operation requires some experience. The fused sodium peroxide at a low red heat will gradually penetrate through the carbonate lining.

If the sample is not thoroughly mixed with the peroxide, or if it is not fused for a sufficient time or at too low a temperature, oxidation will be incomplete. If a bright red heat is used, the crucible is likely to be eaten through.

The error due to the presence of sodium salts has already been mentioned.

Procedure. It is best not to dry this sample more than 2 hours, since some sulfides tend to oxidize slowly at 100° C. Obtain from the storeroom two iron crucibles with covers,[1] and two squares of asbestos. In the center of the latter, cut with a sharp knife a perfectly round hole of such size (38 mm. diameter with the usual size of crucible) that the crucible, when placed in it, projects about 4 mm. above the asbestos, just enough so that the cover rests on the crucible and not on the asbestos. If the hole is too small, do not attempt to enlarge it by pressing the crucible down into it. In this way a sort of collar would be formed around the metal and prevent it from being properly heated. Heat the asbestos with a flame for a minute or two to drive off the volatile matter contained in it. Clean the crucible, using pumice or sand if necessary; dry it and place about 1 g. of sodium carbonate in the bottom of it. If the crucible has been lined with carbonate, do not add any more. Take the crucible to the balance, and weigh into it a 0.5 g. sample of the sulfide; then add to it about 4 g. of sodium peroxide for every half gram of sample. Immediately mix the substances very thoroughly with a warm glass rod. Carbonate and peroxide must never be weighed on the analytical balance, but on the side-table balance. Sodium peroxide must be carefully handled. It is very hydroscopic, and the can or bottle containing it must be kept closed. Peroxide oxidizes organic

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[1] Nickel crucibles are less attacked but are much more expensive.

matter very readily, and must not be allowed to stand in contact with paper, etc. If the powder sticks to the stirring rod, even when warm, due to absorption of moisture by the peroxide, wipe off the rod carefully with a very small piece of filter paper, and add the latter to the crucible. Cover the mixture with a thin layer of peroxide, place the covered crucible in the hole in the sheet of asbestos and just above the top of the burner, and heat it with a very low flame. Sometimes the reaction is quite energetic. Raise the heat gradually until, after 10 minutes, the crucible is at a low red heat, just sufficient to keep the mass completely fused. Remove the cover occasionally and examine the contents. Be sure that no solid crust forms on the sides. A bright red heat will cause the crucible to be badly attacked, perhaps even perforated. Keep the mass fused for 15 minutes to complete the oxidation (Equation (1)). Cool, place the crucible in a 400 ml. beaker, and add enough water to cover the crucible. Keep the beaker covered. The crucible should never be placed directly on the laboratory table because the danger of taking up traces of a sulfate. Rinse off the crucible cover into the beaker. When everything has dissolved out of the crucible, lift the latter out with a glass rod, and wash it off carefully. Do not put rubber-tipped rods into this alkaline solution as they will give up compounds containing sulfur. The excess of peroxide dissolves to form sodium hydroxide and hydrogen peroxide:

$$(13)\quad Na_2O_2 + 2H_2O = 2NaOH + H_2O_2.$$

Dilute the solution to 200 ml. and boil it for a minute or two to destroy the peroxide which decomposes with evolution of oxygen. Stir the solution if it tends to bump. A green shade in the solution is due to the presence of sodium manganate, Na_2MnO_4, the manganese coming either from the sample or from the iron crucible. Such a color indicates that all peroxide has been destroyed. If manganate ion is not present, add a solution of potassium permanganate, drop by drop, while stirring constantly, until a faint green or pink color appears, indicating the absence of peroxide:

$$(14)\quad Na_2MnO_4 + H_2O_2 = MnO_2 + 2NaOH + O_2.$$

Reduce the excess of manganate ion to manganese dioxide by adding a drop of formaldehyde or alcohol and boiling the solution. The object of destroying all peroxide is to prevent it from bleaching the indicator which is to be added.

Stir the precipitate and examine the bottom of the beaker. Undecomposed copper, nickel, or iron sulfide is more dense than the ferric oxide, copper oxide, etc., and quickly settles out as a black powder. If any of this appears, the fusion was not continued long enough, and the sample must be discarded and a new one started. It is not always possible to detect incomplete decomposition in this way, especially in the case of iron pyrites and zinc sulfide, or when the precipitate of oxide itself is black. Do not confuse undecomposed sulfide with scales of black magnetic oxide of iron from the crucible.

The solution is so strongly alkaline that it attacks filter paper. Therefore neutralize a part of the alkali by adding 6 ml. of concentrated hydrochloric acid. Filtration will be hastened if paper pulp is added as described under "Procedure for Iron." Plenty of time must be allowed for filtering and for thorough washing of the precipitate. Let the mixture settle, filter it through a paper filter into an 800 ml. beaker and wash the precipitate 15 times with hot, 1 per cent sodium carbonate solution. Then test a very small portion of the washings for chloride ion, and continue the washing if necessary. If a trace of the precipitate runs through the filter, it will be dissolved when the filtrate is acidified. Add a few drops of methyl orange, sufficient to impart a very light yellow tint to the solution, and add concentrated hydrochloric acid, drop by drop, with constant stirring, until the indicator just turns red, and then three or four drops excess (Equation (3)). If any peroxide is present, it will destroy the indicator. When the solution is made neutral, a precipitate of hydroxide will often form, which will dissolve when a slight excess of acid is added. If a precipitate remains, it must be filtered off and washed. (Why avoid a large excess of hydrochloric acid?) Any silica present will usually remain in solution and will not interfere. The solution which will have a volume of 500-600 ml. is heated to boiling and the sulfate ion is precipitated by the slow addition of barium chloride, as in the determination of sulfur trioxide in a soluble sulfate (Equation (4)). The solution may be allowed to concentrate to 300 or 400 ml. if desired, but not further. Filter and wash the precipitate with hot water, ignite it as before, and weigh as barium sulfate. Calculate the percentage of sulfur (not sulfur trioxide, since there is no oxygen in a sulfide). The factor for converting the barium sulfate into sulfur is 0.1373.

REVIEW QUESTIONS AND PROBLEMS

1. Outline a method for the complete analysis of a complex sulfide of iron, cadmium and manganese.

2. Outline a method for the complete analysis of a complex sulfide of zinc, arsenic and iron.

3. Write equations for the determination of both cadmium and sulfur in cadmium sulfide.

4. A sample of steel weighing 3.000 g. is burned in oxygen and the resulting sulfur dioxide and trioxide are absorbed in 100.0 ml. of 0.01100 *N* sodium hydroxide containing a little hydrogen peroxide. The excess of alkali requires 60.10 ml. of 0.01500 *N* acid. Calculate the per cent of sulfur in the steel.

Ans. 0.107 per cent.

5. Suggest a method for the determination of sulfide and sulfate in a mixture containing ferrous sulfide and basic ferrous sulfate.

6. A sample weighing 1.0690 g. and containing thiocyanate, after fusion with sodium peroxide yields 0.9060 g. of barium sulfate. Calculate the per cent of CNS in the sample.

7. In the volumetric method for sulfur what weight of steel must be taken so that the number of ml. of 0.0500 *N* iodine solution will represent the percentage of sulfur?

8. The sulfur in a sample of Na_2S_x after oxidation to sulfate yields 7.0026 g. of barium sulfate. The same weight of sample requires 20.00 ml. of normal acid to titrate the sodium. What is the formula of the salt?

9. The zinc in a sample weighing 1.0035 g. is precipitated as sulfide and allowed to react with an excess of silver chloride: $ZnS + 2AgCl = \downarrow Ag_2S + ZnCl_2$. To the soluble chloride is added 40.18 ml. of 0.1250 *N* silver nitrate and the excess requires 5.02 ml. of 0.1630 *N* thiocyanate. Calculate the percentage of zinc in the sample.

Ans. 13.70 per cent.

10. Calculate the loss in weight when 1.0000 g. of FeS_2 is ignited in the air to ferric oxide.

11. How much 0.1000 *N* alkali would be neutralized if the sulfur volatilized in problem 10 is oxidized to sulfuric acid?

CHAPTER XVII

QUANTITATIVE SEPARATIONS

Several different principles, both physical and chemical, form the basis of the chief types of analytical separations that have been developed up to the present time; a brief review of the methods is presented here.

SEPARATION BY PRECIPITATION

Electroanalysis. The use of the electric current as a precipitant and as a separating agent is considered in detail in Chapters XIX and XX. Certain metals are very readily precipitated in the metallic form at the cathode of an electrolytic cell and others may be separated as oxide deposits either at the anode or the cathode. The gain in weight of an appropriate electrode is determined after a deposition has been completed.

The Reagent Causes a Single Substance to Precipitate. This type of process is the goal of gravimetric precipitation methods. The ideal of an utterly specific reagent for one kind of ion in the presence of all others is seldom approached, but by making use of group separations along the general lines of qualitative analytical schemes, and by employing prior oxidation, reduction or complex-formation, it is possible to cause a given reagent to precipitate only one kind of ion from a rather complex mixture. For example, nickel in a complex steel or a ferroalloy may be precipitated in the form of its dimethylglyoxime salt, after an oxidizing treatment, removal of silicon as SiO_2, and the transformation of ferric iron into a complex tartrate. The development of specific organic precipitants is further discussed on p. 375.

Assuming that conditions have been discovered under which the principal reaction is the precipitation of a single chemical compound, there remain to be considered effects which cause minor or major contamination of the precipitate thus formed.

Several distinct processes need to be considered and their natures understood. In Chapter XV adsorption has been considered briefly. Some further considerations will be given here, together with a discussion of occlusion and post-precipitation.

Adsorption. Adsorption is defined as an increase in concentration at the interface or surface region between the particles in question and the solution or other medium surrounding them. The adsorption of a dissolved substance by a precipitate follows a kind of distribution law, and at constant temperature the following type of relation was shown by Freundlich[1] to apply to the adsorption equilibrium:

$$X = kC^{1/n} \text{ (adsorption isotherm).}$$

X is grams of substance adsorbed per gram of precipitate, C is the concentration of dissolved substance, k is a constant and n a second constant greater than 1 and frequently close to 2. A typical adsorption isotherm is shown in Fig. 53.

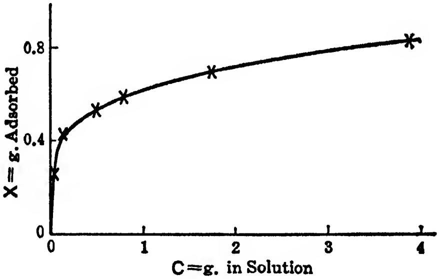

Fig. 53. Adsorption Isotherm. The line is calculated from the equation $X = 0.631 \times C^{1/5}$. The points marked with crosses were determined experimentally for the adsorption of arsenious acid by ferric hydroxide at room temperature. (Biltz, Ber. **37**, 3138 (1904)).

From the parabolic shape of the adsorption isotherms it is apparent that the concentration of a foreign substance that is prone to be adsorbed by a given precipitate should be made as low as possible, e.g., by judicious addition of reagents, etc., and that reprecipitation in order to be effective must be made from a solution in which the concentration of the foreign substances is very low.

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[1] Freundlich, Colloid and Capillary Chemistry, Methuen, 1926.

With regard to the substances that are prone to be adsorbed, it appears from the work of Paneth, Fajans, Hahn and their associates[1] that those ions are most strongly adsorbed by an ionic lattice that form insoluble compounds with one of the ions of the precipitate. Hydrogen ions, because of small size and high ratio of charge to mass, are exceptional and tend to displace other positive ions. The particles tend to adsorb that ion of their lattices that is present in excess, thereby becoming charged. This situation has been pictured in Chapter IX, Fig. 43, and is further described in Fig. 54:

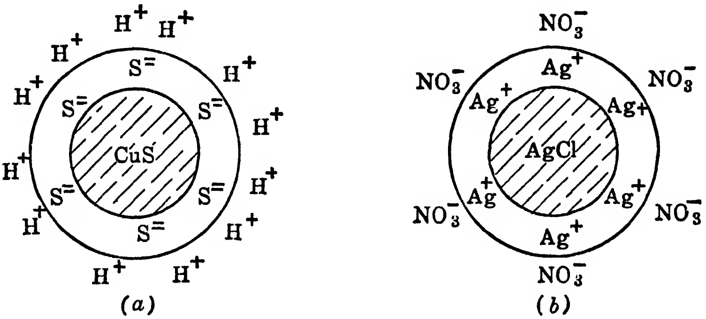

FIG. 54. Primary Adsorption Layers and Layers of Counter Ions. (*a*) Represents a particle of copper sulfide with sulfide ions adsorbed. The hydrogen ions in the secondary or counter layer are more loosely held. (*b*) Represents a particle of silver chloride with a primary layer of adsorbed silver ions, and a secondary or counter-ion sphere of nitrate ions.

With the aid of radioactive elements used as indicators, with various dyes, and by conventional methods of analysis it has been possible to demonstrate exchange of ions in a particle with common ions in the solution, or with other ions (exchange adsorption); also exchange between counter ions and ions in the solution; also adsorption of compounds.[2]

Whenever a colloidal suspension is flocculated, ions are adsorbed, and in analysis this factor is taken care of either by

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[1] For an extensive review of adsorption and the theory of precipitation, with abundant references, see I. M. Kolthoff, J. Phys. Chem. **36,** 860–881 (1932); *ibid.* **40,** 1027 (1936).

[2] Kolthoff, J. Phys. Chem. **40,** 1027 (1936). A review of various work on the types of adsorption above mentioned and others.

arranging to have the adsorbed ions of such nature that they are removed by drying or ignition, or else displaced from the precipitate by a harmless electrolyte during the washing, as has been described on p. 302. These considerations apply to surface adsorption, which is in many cases rather easily counteracted. If the adsorbed material is built in during the formation of the crystals, then there is a more deep-seated contamination called occlusion.

Occlusion as has just been stated is a process of building in adsorbed matter as imperfections in the rather loose structure of crystals as they form. Ions and their sheaths of water molecules are, so-to-speak, captured in the mosaic of crystal blocks. The higher the degree of supersaturation and hence the more sudden the crystallization process, the more foreign material is first occluded. The extent of the contamination may range from a rather minor amount up to mix crystal formation where the foreign substance has ions of proper shape and size to build readily into the lattice.

The process of occlusion is a very significant one from an analytical standpoint. In order to prevent the extent of occlusion from becoming detrimental one may: (a) Transform the foreign material into a state where its tendency to be occluded is less, as for example by reducing ferric to ferrous ion before precipitating the sulfate in a solution containing the two substances. In extreme cases prior removal of the interfering ion is the only available expedient. (b) Control the addition of the reagent and the solubility of the precipitate so that the crystals form slowly under conditions in which they are somewhat soluble, the conditions being further adjusted after the major portion of the precipitate has formed. (c) Allow the precipitate to age or digest, preferably at an elevated temperature. Due to the rather loose structure of the particles there is still possibility of communication being established between the material trapped within the crystal mosaics and the solution. The forces between the ions of the lattice tend to cause the foreign material to be expelled. This process is aided by a certain amount of recrystallization at elevated temperatures. The net result is often a very considerable purification of the particles, coupled with better filtering qualities produced by the cementing together of smaller aggregates into larger ones.

Post-precipitation. Certain long-known instances of contamination were thought to occur during precipitation, e.g., contamination of calcium oxalate by magnesium oxalate; of copper sulfide by zinc sulfide, etc. It is now known that the initial precipitate is quite pure, but that after it has formed, the second substance begins to form on the surface of the first. This process is called post-precipitation to distinguish it from other processes which cause impure precipitates to be obtained. In the case of sulfide precipitates the adsorbed layer of hydrogen sulfide apparently causes the second sulfide to deposit from the supersaturated solution of the more soluble sulfide upon the surface of the first.[1] On the basis of this view Caldwell and Moyer[2] devised a very ingenious and effective method of preventing post-precipitation and thus making much more satisfactory the separation of zinc from cobalt, and of copper from zinc. An aldehyde of structure $RCH{=}CHCHO$ not only becomes adsorbed at the surface of the particles of the sulfide that first precipitates, but also scavenges or cleans the surface of adsorbed hydrogen sulfide by chemical action. In the separation of zinc from cobalt, acrolein was one of the most effective aldehydes, while crotonaldehyde was somewhat more satisfactory than others in the separation of copper from zinc.

In investigating new or unfamiliar processes involving precipitation it should always be kept in mind that *the behavior of the ions toward a given reagent when it is applied to their separate solutions is no guarantee that the same behavior will be exhibited when the substances are present in mixtures.* A totally unexpected contamination may occur when the process is applied to separate one substance from a complex mixture. When the causes have been discovered, a remedy may be found. If not, a new scheme must be evolved, or prior separations must be made. Another alternative is separation by repeated precipitation.

Organic Reagents for Inorganic Ions. A few excellent and rather specific organic reagents for inorganic ions were known and commonly used in the first quarter of the present century,

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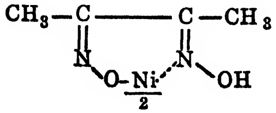
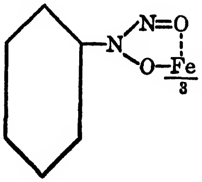
[1] Kolthoff and Pearson, J. Phys. Chem. **36**, 549 (1932), have shown that zinc sulfide though present in supersaturated solution is far more readily deposited at the surface of sulfides of the second analytical group than on other finely divided material.

[2] Caldwell and Moyer, J. Am. Chem. Soc. **57**, 2375 (1935); **59**, 90 (1937).

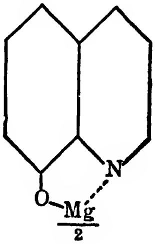
e.g., dimethylglyoxime for nickel, and the rather non-specific "cupferron" reagent (beta-nitrosophenylhydroxylamine ammonium salt) which precipitates not only copper and iron, but very many of the elements of the hydrogen sulfide group, etc. Due to the pioneering work of Feigl[1] this field is undergoing systematic expansion. Among the best of the present reagents are those that form inner complex, or chelate, compounds with the ion that is to be precipitated. A five or six-membered ring is formed, and the compound is in general characterized by distinctive color, very low solubility in water, in which no appreciable ionization of such compounds occurs, but ready solubility in certain organic solvents, e.g., ether. Some typical structures are indicated below:



(a)
Nickel Dimethylglyoxime.



(b)
Cupferron
Precipitate
of Ferric
Iron.



(c)
8-Hydroxyquinoline salt
of Magnesium.

Here Ni/2, Fe/3, Mg/2 indicates that for each valence of the metal a group similar to that shown will be attached to the metal in the compound.

Relatively few reagents have thus far been discovered that are as specific as dimethylglyoxime is for nickel. However the possession of reagents of rather distinctive properties, e.g., 8-hydroxyquinoline which gives a crystalline precipitate of its aluminum salt in acetic acid-acetate buffer solutions, is a decided asset in planning certain methods of analysis. In general the organic precipitants are not so easy to use as inorganic ones because of the difficulty of telling when precipitations are com-

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[1] F. Feigl, Ind. Eng. Chem. Anal. Ed. 8, 401 (1936). Comprehensive review; bibliography. Organic Reagents for Metals, Hopkin and Williams, Ltd., London, 3rd Ed., 1938.

plete, due to the slight solubilities of many of the reagents in water. Because of the characteristics of the precipitates which are apt to be bulky, a semi-micro range of substance to be determined is often essential. This field of work is a rapidly expanding one that is continuing to make many separations easier and more perfect both for qualitative and quantitative purposes.

Fractional Precipitation. Separation of Ions That are Precipitated by the Same Reagent. If the solubility products of two substances that form insoluble salts with the same precipitant are sufficiently far apart, one substance will be substantially completely precipitated before the other begins to form. This principle is used in the Mohr method for titrating chloride with silver ion, using chromate ion as an indicator. In general if two salts have the formulas BA and CA, then at the point where the second one just begins to form, we have $[A^-]$ in equilibrium with both precipitates, and hence:

$$[A^-] = \frac{S_{BA}}{[B^+]} = \frac{S_{CA}}{[C^+]}; \text{ or } \frac{[C^+]}{[B^+]} = \frac{S_{CA}}{S_{BA}}$$

where S_{BA} and S_{CA} are the respective solubility products.

There are not many practical illustrations of this principle, except in the cases of hydroxide and sulfide separations which are easy to control because of the ease of control of hydrogen-ion concentration which is essential to both types of separation. These separations are considered under the next classification.

Precipitations and Separations at Controlled Hydrogen-ion Concentrations, or *p*H. The topic of buffer action has been considered in Chapter VII, p. 129, where the *p*H scale of acidity is also explained. These considerations need to be clearly in mind in the following discussion.

Hydrous Oxides or Hydroxides. Various metallic ions are precipitated in the form of hydrous oxides, or hydroxides, which are seldom free of the anions that are present due to adsorption, occlusion or in some cases precipitation in part as basic salts. The *p*H values at which precipitation begins depends somewhat upon the anion that is present and also upon the concentration of the metallic ion. The approximate *p*H values at which precipitation begins are assembled in Table XVIII, p. 378.

It can be shown by a simple calculation that the presence of a very moderate quantity of ammonium chloride will buffer the

TABLE XVIII. VALUES OF pH AT WHICH VARIOUS HYDROXIDES PRECIPITATE[1]

pH	
11	Mg^{++}
10	
9	Ag^+; Mn^{++}; Hg^{++}
8	Co^{++}; Ni^{++}; Cd^{++}
7	Fe^{++}
6	Zn^{++}; Cu^{++}
	Cr^{+++}
5	Al^{+++}
4	
3	
2.2	Fe^{+++}
2	TiO^{++}

action of ammonium hydroxide so that the solubility product of magnesium hydroxide is not reached in 0.05 M magnesium solution that is 0.1 M in ammonium hydroxide. About 0.6 g. of ammonium chloride per 100 ml. of solution is theoretically required. Iron and certain other hydrous oxides may be separated by fractional precipitation in this manner. Owing to adsorption and other effects, a reprecipitation is commonly necessary to make the separation quantitative.

The neutralization of a solution by the addition of a base drop by drop necessarily produces local excesses of the base in the zone of mixture with the solution. Very much sharper separations are made by the slow liberation of ammonia uniformly through the solution by the hydrolysis of urea added for the purpose. This method which was devised by Willard and Tang, has been described on p. 349.

Amphoteric hydroxides have both basic and acidic ionization constants. For example, aluminum hydroxide ionizes in the two fashions:

$$AlO(OH) \rightleftharpoons AlO^+ + OH^-$$

$$AlO(OH) \rightleftharpoons AlO_2^- + H^+.$$

The optimum pH for precipitation depends upon the relative magnitudes of the two constants. If they are equal, the minimum solubility is at $p\text{H} = 7$. In this case the minimum solubility is from pH 6.5 to 7.5, with initial precipitation between 4 and 5. At pH 8-9 the precipitate begins to dissolve. Blum[1] found that methyl red was a suitable indicator, changing from red to yellow

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[1] After Britton, Hydrogen Ions, Van Nostrand, 1929, p. 278, with incorporation of more recent values for Fe^{+++} and TiO^{++}.

[2] Blum, J. Am. Chem. Soc. 38, 1282 (1916).

at the point of complete precipitation in hot solution. Ammonium chloride or nitrate is added for buffering purposes.

Basic Salts. Acetates; Benzoates. These separations depend upon the extensive hydrolysis of the acetates or benzoates of ferric iron, chromium and aluminum at elevated temperatures, while those of manganese, etc., are not much hydrolyzed. The increased ionization of water supplies hydroxyl ions, and the hydrogen ions that are formed simultaneously combine in large measure with acetate or benzoate ions because the solution is buffered by an excess of alkali acetate or benzoate. The critical part of the procedure is the adjustment of the *p*H before the hydrolytic action.[1] In the urea method (preceding section) the *p*H of the solution is adjusted to a value that is safely below the limits for precipitation of the substance desired. Upon heating, the *p*H is very uniformly and gradually changed to the precipitation range in which it is kept practically static for an adequate period by the buffering action of the salts added for this purpose.

Sulfide Precipitations. The control of sulfide ion concentration by control of the acidity, or *p*H, of the solution is stressed in schemes of qualitative analysis. Both of the ionization constants of hydrogen sulfide are very small:

$$\frac{[H^+][HS^-]}{[H_2S]} = K_1 = 5.7 \times 10^{-8}; \frac{[H^+][S^=]}{[HS^-]} = K_2 = 1.2 \times 10^{-15}$$

and

$$K_1 \times K_2 = \frac{[H^+]^2[S^=]}{[H_2S]} = 6.8 \times 10^{-23}.$$

Combining the last expression with that for the solubility product of a sulfide, $[B^{++}][S^=] = S_{BS}$,

$$[B^{++}] = \frac{S_{BS}}{[S^=]} = \frac{S_{BS}[H^+]^2}{6.8 \times 10^{-23}[H_2S]}$$

In a solution 1 *M* in H^+, the solubility of hydrogen sulfide is about 0.1 *M* at room temperature. In accord with experience

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[1] Furman and Low in unpublished work found that in case of iron the *p*H of the cold solution should be 4.7 to 5.3 before hydrolysis. P. Wenger (cf. Chem. Abs. **28**, 3335 (1934) found an upper limit of *p*H 6 and an optimum of 4.2.

this expression indicates adequate solubility of MnS, FeS and the like for separation from CuS, CdS, PbS, etc. Zinc, cobalt and nickel sulfides at the customary analytical concentrations are indicated to be borderline cases. As has been stated, zinc sulfide tends to post-precipitate on the surface of copper sulfide because of the adsorbed hydrogen sulfide. Cf. p. 375.

Rigorous calculations based on the solubility product principle are apt to lead to erroneous conclusions, especially in the case of higher sulfides, e.g., As_2S_5, Sb_2S_5, MoS_3, etc. For example, McCay[1] and associates have shown that arsenic acid and hydrogen sulfide react in a very complicated manner to give unstable intermediate sulfoxy acids: H_3AsO_3S, $H_3AsO_2S_2$, and H_3AsOS_3, each of which decomposes into characteristic products; a mixture of As_2S_5, As_2S_3 and S is formed unless the process is carried out at high temperature (100° C.) and acidity in a pressure bottle where, by making use of equilibrium principles, nearly pure As_2S_5 is formed (some sulfur also forms from the action of air on H_2S).[2] The pressure bottle technique does not prevent molybdenum from giving a partial yield of products in a state of oxidation lower than six.

It is by no means certain that sulfide ion is an important reactant in acidified solutions. The concentration of hydrosulfide ions, SH^-, is very considerable and this ion is probably active in the precipitation process.[3] Intermediate products, e.g., $Hg(SH)_2$, Cl-Hg-S-Hg-Cl, and others may participate in the processes.

The effect of *p*H upon the precipitations of sulfides has received a considerable amount of detailed study.[4] The precipitation of zinc as the sulfide from a buffered sulfuric acid medium has long been practiced. The *p*H of various buffers consisting

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[1] McCay, Am. Chem. J. **10,** 459 (1888); Z. anorg. allgem. Chem. **29,** 36 (1910); J. Am. Chem. Soc. **24,** 661 (1902); McCay and Foster, Z. anorg. allgem. Chem. **41,** 452 (1904).

[2] McCay, Am. Chem. J. **9,** 174 (1887).

[3] G. M. Smith, J. Am. Chem. Soc. **44,** 1500 (1922); **46,** 1325 (1924); Feigl, Z. analyt. Chem. **65,** 25 (1924).

[4] Solubility products of sulfides, Kolthoff, J. phys. Chem. **35,** 2711 (1931). *p*H ranges: For ZnS, 2–3 and higher, Fales and Ware, J. Am. Chem. Soc. **41,** 487 (1919). For CoS, 3.7 and higher, Haring and Leatherman, J. Am. Chem. Soc. **52,** 5135 (1930). For NiS, 4.4 and higher, Haring and Westfall, ibid. **52,** 5141 (1930).

of mixtures of $NaHSO_4$ and Na_2SO_4 and the proper conditions for precipitations and separations have been established by Jeffreys and Swift.[1] If the molar ratio of $NaHSO_4$ to Na_2SO_4 is about 1 : 3 with a total concentration of the two sulfates equal to about 0.35 molar, the zinc is substantially completely precipitated and effectively separated from Ni, Fe, Mn, Cr and Al. For the conditions above stated the initial *p*H is 1.78 and the final *p*H is about 1.6, which is probably the safe upper limit of acidity. At *p*H 1.54 about 1 mg. of zinc remains unprecipitated in a solution of 250 ml. volume. If 0.13 mole of KCl is added to 250 ml. of a solution, prepared as has been indicated, from 1.5-2. mg. of zinc remains unprecipitated. The presence of chloride increases the acidity or lowers the *p*H, as was shown by electrical measurements, and also tends to form a complex.

Carbonates. There must obviously be an upper limit of acidity which may not be exceeded if a carbonate is to remain undecomposed. On the other hand, amphoteric elements are not completely precipitated as carbonates in solutions that are too alkaline. For example, lead carbonate is incompletely precipitated if an excess of sodium carbonate is added to the solution of a lead salt. Complete precipitation is obtained from an ammonium carbonate-ammonia solution. Carbonate precipitation finds only limited use in quantitative analysis, one of the chief instances being the use of an ammonium carbonate-ammonia mixture to remove the major part of the calcium that is present, prior to the estimation of sodium and potassium.

Double Ammonium Phosphates. Magnesium ammonium phosphate has a minimum solubility in a solution containing 2.5 per cent of NH_3, or at an estimated *p*H of about 11.5-11.7. The optimum *p*H for complete precipitation of manganese ammonium phosphate is only known empirically to be slightly on the alkaline side of 7. In the case of zinc ammonium phosphate the optimum range is *p*H 6.4 to 6.9, 6.6 being the best value.[2] The solution in this case is buffered with diammonium phosphate, $(NH_4)_2HPO_4$, and ammonium or sodium acetate; 5-10 g. of ammonium chloride may be present per 150 ml. of solution.

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[1] Jeffreys and Swift, J. Am. Chem. Soc. **54**, 3219 (1932).

[2] Ball and Agruss, J. Am. Chem. Soc. **52**, 120 (1930).

SEPARATION BY EXTRACTION

The process of extraction of a single substance from a solution by shaking the solution with several small portions of an immiscible solvent is a very commonplace operation in organic preparative work. In analytical chemistry extraction is used as a method of indication in many volumetric processes involving the formation or consumption of iodine. See p. 282. The same general technique is finding increasing uses in separations. The principle of the method is that of distribution which follows the law that the ratio of the concentrations of a substance in the two solvents is a constant, provided association or dissociation of the substance does not occur in either solvent: $\frac{C}{C_1} = K$ at constant temperature, where C is the concentration in one solvent, for example the non-aqueous layer, and C_1 that in the other layer. If ionization occurs in the aqueous layer the formula is modified to allow for the effect of ionization:

$$\frac{C}{C_1(1-\alpha)} = K, \text{ where } \alpha \text{ is the degree of ionization.}$$

Illustration of the principle. At 18° C. the distribution constant of iodine between water and carbon bisulfide is 420.[1] Suppose a solution of 0.018 g. of iodine in 100 ml. of water were shaken with two 50 ml. portions of carbon bisulfide. To calculate the concentration of the iodine remaining in the aqueous layer, assuming that neither association nor ionization takes place. Let x be the weight of iodine in the CS_2 layer.

Then $$\frac{\frac{x}{50}}{\frac{0.018 - x}{100}} = 420. \; x = 0.01791 \text{ g.}$$ Then 0.00009 g. remains in the aqueous layer. Upon a second extraction

$$\frac{\frac{x'}{50}}{\frac{0.00009 - x'}{100}} = 420, \text{ and } 0.00009 - 0.0000895 = 0.0000005 \text{ g.}$$

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[1] Berthelot and Jungfleisch, Ann. Chim. Phys. (4) **26**, 396 (1872).

of iodine remains in the water. In general the final amount remaining after *n* extractions of a volume *V* ml. containing *w* grams with portions of volume *V'* of immiscible solvent is: Final

$$\text{Wt} = w\left(\frac{V}{KV' + V}\right)^n.$$

Extractions with Ethers. Common, or diethyl ether, extracts ferric chloride and certain other substances from aqueous solutions that are 6.2-6.34 *M* in hydrochloric acid.[1] In this way ferric iron may be separated from Al, Cr^{III}, Mn, Ni, Co and Ti. The following table gives a summary of the possibilities of this method:

Table XIX. Extraction of Chlorides by Ether[2]

Element	Per Cent Extracted	Element	Per Cent Extracted	Element	Per Cent Extracted
Al	0	In	Trace	Rh	0
Sb($SbCl_3$)	6	Ir ($IrCl_4$)	5	Se	Trace
Sb($SbCl_5$	81	Fe($FeCl_3$)	99	Ag	0
As($AsCl_3$)	68	Fe($FeCl_2$)	0	Te($TeCl_4$)	34
Be	0	Pb	0	Th($ThCl_4$)	0
Bi	0	Mn	0	Tl($TlCl_3$)	90–95
Ca	0	Hg($HgCl_2$)	0.2	Sn($SnCl_4$)	17
Cd	0	Mo(MoO_3)	80–90	Sn($SnCl_2$)	15–30
Cr	0	Ni	0	Ti	0
Co	0	Os	0	W(with PO_4)	0
Cu	0.05	P(P_2O_5)	Trace	U	0
Ga	97	Pd($PdCl_2$)	0	V(V_2O_5)	Trace
Ge	40–60	Pt($PtCl_4$)	Trace	V(V_2O_4)	Trace
Au($AuCl_3$)	95	Rare earths	0	Zn	0.2
				Zr	0

Isopropyl ether is a more convenient extraction liquid for certain uses, and the acid concentration is not quite so critical as with ethyl ether.[3] It was found the iron could be separated from numerous other elements by an automatic extraction apparatus, provided the solution was shielded from light during the

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[1] Speller, Chem. News, **83,** 124 (1901).

[2] After E. H. Swift, J. Am. Chem. Soc. **46,** 2375 (1924); Hillebrand and Lundell, "Applied Inorganic Analysis."

[3] Dodson, Forney and Swift, J. Am, Chem. Soc. **58,** 2375 (1936).

extraction.[1] Dichloroethyl ether is an especially effective solvent for ferric chloride in solutions 9 M or more in hydrochloric acid.[2]

Other Extraction Methods. The selective extraction of salts from anhydrous mixtures by means of solvents has been described briefly on p. 296. The use of selective organic reagents in extraction procedures is a rather new field of analysis. This type of procedure may be illustrated by mention of the dithizone extraction method for recovering traces of lead from extracts such as washings of fruit suspected of containing traces of spray residues. By adjusting the pH of the aqueous layer and adding cyanide to the ammoniacal solution to form complexes of copper and certain other metallic ions, a solution of dithizone (diphenylthiocarbazone) in chloroform, extracts only stannous, bismuth and lead ions in the form of red complexes with the reagent.[3] One part of lead in 20 million parts of solution can be detected by this method; it is so sensitive that difficulty is often found in freeing the glassware and the reagents sufficiently from lead to get a small blank test.

SEPARATIONS BASED UPON VOLATILIZATION

The use of evaporation, sublimation and distillation procedures for the separation of more volatile from less volatile substances is important in analysis as well as in other fields of chemistry.

Volatilization. The loss of volatile material at a definite temperature is one of the simplest means of separating a given class of substances from others. Drying at 100° C. generally gives a separation of inorganic powders from loosely bound water. Occluded water and water of constitution, or essential water, e.g., in $MgHPO_4$, ($2MgHPO_4 \rightarrow Mg_2P_2O_7 + H_2O$), are evolved at elevated temperatures, the exact range being a question of experimental test in a new or unfamiliar case.

Processes of volatilization and of chemical evolution of gases may be made substantially complete by sweeping out the volatile substances by a stream of indifferent gas, and the residue may

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[1] Ashley and Murray, Ind. Eng. Chem. Anal. Ed. **10**, 367 (1938).

[2] Axelrod and Swift, J. Am. Chem. Soc. **62**, 33 (1940).

[3] Method of Fischer and Leopoldi. For literature references see Scott's Standard Methods, 5th Ed., p. 521, D. Van Nostrand Co., 1939.

be weighed, or alternatively the volatile product may be recovered chemically or physically (e.g., by condensation at a low temperature) and its weight determined. The carbon dioxide of a carbonate is evolved upon addition of a suitable acid, and the carbon dioxide is absorbed in an alkaline reagent, e.g., sodium hydroxide—asbestos pellets ("ascarite"), and the gain in weight is found. See p. 402. The determination of carbon in steel or in organic compounds is, of course, made by combustion of the carbon to carbon dioxide and absorption of the latter as has been described. The evolution of ammonia followed by absorption and titration of the excess of standard acid has been described on p. 157.

Distillation. The theory of fractional distillation is discussed in various texts on physical chemistry. The process finds few applications in inorganic analysis. It is one of the few available methods for separating certain mixtures of hydrocarbons in gas analysis.

An inorganic illustration is the separation of arsenic, antimony and tin in the form of their chlorides. Arsenious chloride distils off first and the antimonous chloride is held back if a proper fractionating column is used. During the distillation of the antimony chloride the tin is held back by the addition of phosphoric acid. Finally upon adding a bromide it is possible to distill out the tin.[1]

The water in bulky materials, e.g., grain, petroleum products, etc., is distilled out by heating the material with a solvent or liquid that is immiscible with water, e.g., xylene, toluene, etc. The water is condensed and determined by measuring its volume.[2]

SEPARATION BY ADSORPTION

(a) *Intentional coprecipitation.* It has long been known that metastannic acid will remove phosphoric acid quantitatively from a solution if the ratio of tin to phosphoric acid is sufficiently high. In certain of the older schemes of qualitative analysis, after a separate test for tin had been made, it was added if not

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[1] A review of prior literature and experimental details are given by Scherrer, J. Research Natl. Bur. Standards, **16**, 253 (1936).

[2] See Scott's Standard Methods, p. 1340, 5th Ed., D. Van Nostrand Co., 1939.

already present in order to remove the phosphate. Freshly precipitated ferric hydroxide collects arsenate and antimonate and is used for this purpose in removing small amounts of these elements from a solution containing a very large amount of copper. If it is desired to work with an acidified solution the impurities may be collected upon manganese dioxide as an adsorbing medium, the manganese being intentionally added and caused to precipitate by oxidation to the quadrivalent state.

(b) *Chromatographic Adsorption.* If a solution is poured through a column of suitable material, e.g., calcium carbonate, activated alumina, etc., there may be selective adsorption and partial fractionation of the various substances into adsorbed layers slightly separated. Upon following the original solution by a proper developing solution, the different substances may be caused to spread down the column into layers visibly separated if the substances are colored. With colorless substances the column may be tested by use of ultraviolet light if the substances have suitable fluorescent properties, or by removing the compact column intact, and locating the various layers by chemical tests. The various portions of the column are separated mechanically and the individual substances recovered by appropriate treatment.

The chromatographic method has long been used in botanical investigation and in organic preparative work.[1] A column of activated alumina has been used in the qualitative analysis of solutions for inorganic ions.[2] There appears to be possibility of a considerable further development of these methods both along qualitative and quantitative lines.

Review Questions and Problems

1. List the chief difficulties that are encountered in the quantitative precipitation of a single kind of ion from a complex mixture, together with the corresponding method for avoiding each difficulty.

2. If $S_{AgCl} = 10^{-10}$ and $S_{AgI} = 10^{-16}$, how completely should iodide

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[1] L. Zechmeister and L. v. Cholnoky, Die chromatographische Adsorptionsmethode, 2nd Ed., J. Springer, Vienna, 1939.

[2] G. Schwab and K. Jockers, Angewandte Chem. **50**, 546 (1937); Naturwissenschaften, **25**, 44 (1937); G. Schwab and G. Dattler, Angew. Chem. **50**, 691 (1937); **51**, 709 (1938). G. Schwab and A. N. Ghosh, *ibid.*, **52**, 668 (1939); H. Erlenmeyer and H. Dahn, Helv. Chim. Acta, **22**, 1369 (1939).

ion be removed before chloride ion begins to precipitate as silver chloride if the chloride ion concentration is 0.01 *M*?

Ans. The concentration of the soluble iodide is 10^{-8} *M* (about 0.001 mg. per liter).

3. What practical difficulties might be encountered in attempting to make quantitative the separation calculated in Problem 2?

4. Given $S_{ZnS} = 7 \times 10^{-26}$ and $S_{FeS} = 3.7 \times 10^{-19}$, calculate whether a separation of the two metals should be possible by hydrogen sulfide.

5. (*a*) What is the final concentration of dissolved zinc in a solution that is 0.1 *M* in H_2S at a *p*H of 2.5? (*b*) Will any ferrous sulfide be precipitated from a solution 0.1 *M* in Fe^{++}, 0.1 *M* in H_2S at a *p*H of 2.5?

Ans. (*a*) 7×10^{-8} *M*. (*b*) Ferrous sulfide should not precipitate until the $[Fe^{++}]$ is 0.37 *M*.

6. Write equations for the equilibria that might be important when a little calcium carbonate is treated with a fairly concentrated boiling solution of ammonium chloride. What bearing have these processes upon the problem of separating and washing calcium carbonate?

7. Summarize the advantages of the urea method of neutralizing a solution as contrasted with the slow addition of dilute ammonia solution.

8. (*a*) Given $S_{Mg(OH)_2} = 1.2 \times 10^{-11}$, at what *p*H will magnesium hydroxide precipitate from a solution 0.005 *M* in magnesium ion? (*b*) Will precipitation of magnesium hydroxide occur when a solution is 0.005 *M* in magnesium ion, 0.01 *M* in ammonium hydroxide and 0.01 *M* in ammonium ion?

Ans. (*a*) *p*H is 9.7; (*b*) *p*H is 9.24.

9. Given $S_{Fe(OH)_2} = 10^{-14}$, calculate how completely ferrous hydroxide may be precipitated before the precipitation of magnesium hydroxide should begin in a solution 0.01 *M* in magnesium ion.

10. Assuming the distribution coefficient for stannic chloride to be $\frac{C_{ether}}{C_{acid}\,6\,N} = 0.2$, calculate how much tin would remain in 100 ml. of 6 *N* acid that originally contained 0.1 g. of stannic tin, after extraction with four 25 ml. portions of ether.

Ans. 0.0822 g.

11. Repeat the calculation of problem 10 for the case of 0.1 g. of ferric iron in 100 ml. of the acid; the constant $\frac{C_{ether}}{C_{acid}} = 99$ in this case.

CHAPTER XVIII

GRAVIMETRIC SEPARATIONS

Methods for the precipitation of a number of different ions were studied in Chapter XVI. The filtrate in each case was discarded and interfering substances were absent. The possibility of using the methods described in that chapter as separations from other anions and cations was discussed. In the analysis of more complex materials such as limestone and brass, certain separations must be carried out, and the filtrate from one precipitate must be used for the precipitation of another substance. In such separations special care must be taken to avoid the slightest loss of filtrate while filtering and washing the precipitate, and to be certain that the precipitate does not retain any of the other substances to be determined. Sometimes the latter condition can not be realized and the precipitate must be dissolved and reprecipitated. When this procedure is not effective as a means of obtaining a pure precipitate and of recovering in the filtrate all ions which are to be determined subsequently, the separation is unsatisfactory and another method must be used. The form in which an ion is precipitated is not necessarily the form in which it can be weighed. Thus, calcium is precipitated as the oxalate but it is weighed as the carbonate or the oxide. In Chapter XV a list is given of the forms in which various elements are commonly weighed, but a number of the methods suggested in that table are not applicable to separations of the elements in question from many other elements.

The errors of occlusion and adsorption, and those due to incomplete washing and to careless technique in general, are now even more serious. Not only do they cause an error in the determination of one substance but also in the subsequent determinations. To avoid such errors the student must therefore use all the skill which he has acquired in the preceding work. Carelessness may result in the loss of a solution from which one or more substances have already been separated, and may thus necessitate the repetition of much preliminary work with a consequent loss of time.

It is preferable to precipitate directly the substance to be determined, because such a procedure results in a saving of time and in a decrease in the possibility of error. As already pointed out, this method is impossible in a large proportion of cases.

Limestone, monel metal, brass, and German silver are common materials, the analysis of which gives excellent practice in the separation of various elements. Complete procedures for these materials are included in this chapter and in Chapter XX.

THE ANALYSIS OF LIMESTONE

Limestone, which is essentially calcium carbonate, is found in a very pure form as calcite, but it more often contains magnesium, in amounts which vary from traces up to that present in dolomite, $MgCa(CO_3)_2$. Limestone may also contain small amounts of silica, iron, aluminum, titanium, manganese, sulfur, phosphorus, potassium, sodium, and organic matter. The silica may be present as quartz, or as an insoluble silicate, such as clay or feldspar. The sulfur may occur as pyrites, FeS_2, or gypsum, $CaSO_4 \cdot 2H_2O$. The various metals are usually present as oxides or carbonates; potassium and sodium generally as feldspar, which is a potassium, sodium, aluminum silicate.

Since limestone is a material which has so many uses, its analysis is a problem frequently encountered. A complete analysis, involving the determination of all of the substances just mentioned, is a rather long and complicated operation, and is in many cases unnecessary. A shorter "proximate analysis" will often give all the information required. In this shorter analysis some of the oxides are weighed together, no attempt being made to separate them, and some of the elements, such as potassium, sodium, and sulfur, are not determined at all. The proximate analysis ordinarily includes the following determinations all of which are made on the same sample:

1. Loss on ignition. This consists mostly of carbon dioxide with a slight amount of water; sometimes a small loss due to the oxidation of organic matter is included. Ferrous carbonate on ignition is oxidized to ferric oxide, and any sulfide is oxidized to a sulfate.

2. Silica (impure).
3. "R_2O_3," a common term for the combined oxides resulting from the ignition of the precipitate obtained by ammonia and consisting of Al_2O_3, Fe_2O_3, TiO_2, P_2O_5 (as aluminum phosphate or ferric phosphate), Mn_3O_4 and a trace of SiO_2. Only a part of the manganese is precipitated, unless an oxidizing agent is present.
4. Calcium oxide.
5. Magnesium oxide.

Separate samples are used for the following determination:

6. Carbon dioxide.

These determinations must be carried out with the same care employed in a complete analysis. The term "proximate analysis" implies no decrease in precision.

Determination of Loss on Ignition. Since this process consists mainly in the ignition of calcium carbonate to calcium oxide, the procedure is practically the same as that already described under the determination of calcium oxide in calcium carbonate (p. 343). From the percentage of loss an idea of the relative amounts of calcium and magnesium in the limestone may be obtained, if the amounts of insoluble matter and of "R_2O_3" are known. Sometimes, however, the oxidation of organic matter is responsible for a part of the loss. Ferrous carbonate, if present, loses carbon dioxide but this loss is partially offset by the oxidation of the residue to ferric oxide.

Procedure. Weigh a clean porcelain crucible with cover. Add to it from a weighing bottle about 1 g. of the dried limestone and weigh again. Place the covered crucible in a triangle supported in a covered clay cylinder of the type already described (p. 343). Heat the sample slowly at first to avoid mechanical loss from the sudden evolution of carbon dioxide (which may occur with limestone), and then to the full temperature of the Meker burner for one hour. Cool and weigh. Repeat the ignitions for one hour periods until the weight of the residue is constant to 0.2-0.3 mg. Observe all the precautions given under the determination of calcium oxide in regard to ignition and weighing. Calculate the percentage of loss on ignition.

Determination of Uncorrected Silica.[1] The silica in limestone may be present either free or in the form of an insoluble silicate. If any of the latter is present, the residue left after dissolving the limestone directly in hydrochloric acid will not be silica, but a silicate. It has already been stated (p. 356) that insoluble silicates may be rendered soluble by ignition with a strong base such as the carbonate or oxide of sodium, potassium, barium, strontium, or calcium. In the above process of determining loss on ignition, any insoluble silicates are therefore rendered basic by the ignition with the large excess of calcium oxide already present in the sample. The amount of silica in most limestones is quite low, but in exceptional cases where the sample is very impure the proportion of calcium oxide may be insufficient, so that a little sodium carbonate will have to be added. Even when the loss on ignition is not required, a short preliminary ignition of the sample is desirable to render it easily soluble in hydrochloric acid.

The determination of silica is carried out as described under the "Determination of Silica in a Basic Silicate," p. 360, and all of the precautions given there should be observed. In limestone, however, the percentage of silica will be much lower, sometimes less than 1 per cent. After one dehydration, the residue may be taken up with acid and filtered. The filtrate must be dehydrated for a second recovery of silica unless the amount first separated was only 5 or 10 mg. The errors in the process are the same as those already discussed, but in this case it must be remembered that they affect not only the silica determination, but also the succeeding determinations. Dehydration by perchloric acid may also be used if preferred.

Procedure. To save time it is advisable to use separate samples for the determination of loss on ignition. Weigh three other samples of approximately 1 g. of the dried limestone into clean porcelain crucibles with covers, and ignite in the covered crucibles, slowly at first and then at the full heat of the Meker burner, for about ½ hour (observing the precautions in ignition given under this determination) before transferring the residue to 150 ml. beakers and proceeding as directed below. If the residue from the determination of loss on ignition is to be used for the

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[1] The procedure for corrected silica is given on pp. 407-408.

determination of silica, transfer it carefully to a 150 ml. beaker. Add to the small residue in the crucible a few ml. of 1 : 1 hydrochloric acid, heat the mixture for a few minutes to dissolve any adhering particles, and rinse this solution into the beaker. Add 15 ml. of concentrated hydrochloric acid and 1 ml. of concentrated nitric acid (why?); rotate the liquid to get the sample in suspension. Keep the volume of liquid small in order to save time in evaporation.

When the sample has dissolved, except for silica, rinse down the sides of the beaker, evaporate the solution to dryness, and dehydrate the residue as previously directed under the determination of silica, p. 360. Take care to avoid too high a temperature during dehydration. Use a low temperature electric hot plate or a steam bath. Moisten the residue with 4 or 5 ml. of concentrated hydrochloric acid, warm the mixture, and allow it to stand 5 minutes to dissolve basic salts. Add 10-15 ml. of water, and carefully rub loose with a rubber-tipped rod all silica from the sides and bottom of the beaker. Break up any lumps with a stirring rod. Cover the beaker and heat the solution until everything except the silica has dissolved; do not prolong the period of heating unnecessarily. Filter and wash the silica with 1 per cent hydrochloric acid (why not water?), and then with water. Evaporate and dehydrate the filtrate for a second recovery of silica. Ignite the two precipitates together; raise the temperature finally to the full heat of a burner of the Meker type. The precipitate should be white, although it usually contains from 1 to 3 mg. of the oxides of aluminum, iron, and titanium. (How could the total amount of impurity be determined?) Calculate the percentage of impure silica.

Considerable time can be saved in the determination of silica by dehydrating with boiling 70 per cent perchloric acid,[1] as mentioned on p. 357, instead of by evaporation to dryness. Fish and Taylor[2] have also pointed out the advantages of this method in the analysis of limestone and have described the procedure. Perchlorates do not interfere with the determination of the other constituents.

Procedure for Dehydration by Means of Perchloric Acid. Dissolve the sample of limestone which has previously been

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[1] Willard and Cake, J. Am. Chem. Soc. **42**, 2208 (1920).

[2] Fish and Taylor, J. Chem. Education **10**, 246 (1933).

ignited for at least half an hour, in a mixture of 40 ml. of water and 20 ml. of perchloric acid (70-72 per cent). Evaporate the solution on the hot plate until dense, white fumes of perchloric acid appear and boil gently in a covered beaker for 30 minutes, so as not to lose much of the acid. The hot mixture must not be allowed to become solid. After it has cooled add water until the volume is about 100 ml. The presence of a few ml. of hydrochloric acid is often beneficial. Heat the solution to boiling and filter through ashless filter paper.

Wash the paper and the silica precipitate at least *15 times* with 5-10 ml. portions of one per cent hydrochloric acid. and finally with *at least 5* portions of hot water. Be sure to wash the top of the paper thoroughly because it seems difficult to remove all the perchloric acid. To be sure that all perchloric acid has been washed out, the twentieth and final washing should be tested for acidity with litmus paper. Transfer the paper and precipitate to a weighed porcelain crucible and dry the paper above a burner. Lower the crucible, char the paper, burn it off in the usual manner, ignite at the full heat of a burner of the Meker type for 20 to 30 minutes, cool and weigh as impure silica.

Warm, concentrated perchloric acid with organic matter forms a violently explosive mixture. The washing of the paper and precipitate must be very thorough and care should be taken during the drying and charring of the filter paper. The presence of perchloric acid in the paper causes deflagration and consequent loss of precipitate when heated. *The paper must never be placed in the drying oven.*

Determination of "R_2O_3" or Combined Oxides. The errors of this process have been discussed in the section dealing with the determination of iron, pp. 346-347. Note particularly the errors caused by a large excess of ammonia, the solubility of hydrous aluminum oxide in ammonia, the solution of silica from the glass, and the formation of some ammonium carbonate, resulting from the presence of carbon dioxide in the air, which causes calcium carbonate to be precipitated. The last error increases with the concentration of ammonia or of calcium salts, and with the time of standing. Even when every precaution is used, the precipitated hydrous oxides are never free from calcium and magnesium, and must always be dissolved and reprecipitated. Any silica not previously removed will be carried down more or less by this precipitate. If manganese is present, it is advisable to add a few drops of bromine or chlorine water or of pure hydrogen peroxide before making the solution alkaline, in order that all of the manganese may be precipitated as hydrous manganese dioxide. The precipitate consists mainly of hydrous ferric and aluminum oxides, with a little hydrous titanium oxide, because most rocks contain a little titanium. A very small portion of these oxides is present as an impurity in the silica previously removed. If manganese is not completely precipitated at this point, a little of it will come down with the calcium oxalate, and the rest with the magnesium precipitate.

Procedure. If the filtrate from the silica does not contain at least 10 ml. of concentrated hydrochloric acid, add 5 g. of ammonium chloride in order to have sufficient ammonium ion present to avoid the precipitation of magnesium hydroxide. To the solution, 150-200 ml. in volume, add, if manganese is present, a little bromine water or pure hydrogen peroxide, heat the solution, and add filtered, concentrated ammonium hydroxide in slight excess. The color due to bromine disappears as soon as the solution becomes alkaline. Boil the solution a minute or two, and let it stand 10 or 20 minutes until the hydrous oxides coagulate, but no longer. (Why?) The steam should have a perceptible but very faint odor of ammonia. Test the solution with litmus paper. The precipitate may contain hydrous aluminum, ferric, and titanium oxides, hydrous manganese dioxide, aluminum phosphate, and always a little calcium and magnesium hydroxides or carbonates. Filter through a paper filter into a 600 ml. beaker and wash the precipitate 4 or 5 times with hot one per cent ammonium nitrate. Place the original beaker under the funnel and dissolve the precipitate by carefully dropping around the edge of the filter boiling, dilute hydrochloric acid—4 ml. of concentrated acid and 20 ml. of water. Wash the filter with hot, 1 per cent hydrochloric acid, and then with water; dilute the filtrate, if necessary, to 75 ml. and make a second precipitation of the hydrous oxides as before. Take care to avoid a large excess of ammonia. A little filter paper pulp may be used in this second precipitation if desired. Filter through the same filter that was used in the first precipitation, and allow the filtrate and washings to run into the beaker containing the first filtrate. Acidify this filtrate with hydrochloric acid. Label the beaker and commence the evaporation process as directed under the procedure for calcium, p. 395, or p. 397, if the alternative method is to be used.

Wash the precipitate 7 or 8 times with 1 per cent ammonium nitrate solution, fold together the damp filter, place it in a weighed porcelain crucible, and burn off the carbon at a low heat. Finally ignite at a bright red heat, while having the crucible in a slanting position to secure free access of air to the precipitate. (Why?) Cool and weigh as "R_2O_3." This residue may contain Fe_2O_3, Al_2O_3, TiO_2, Mn_3O_4, P_2O_5 (as aluminum phosphate) and a trace of SiO_2. All the phosphorus in the limestone will ordinarily be present in this precipitate. Calculate the percentage of "R_2O_3" or combined oxides.

There are several ways to determine each of the constituents in the precipitate, when necessary. The iron may be determined by titration. (How should the precipitate be dissolved, since hydrochloric acid is without action?) By fusing the precipitate with sodium carbonate and treating the flux with water, a solution of sodium aluminate and sodium phosphate, and a precipitate of ferric oxide and titanium oxide would be obtained. Any manganese would form a green manganate readily reduced to manganese dioxide. The separation of iron, aluminum, and titanium from manganese may be accomplished by the "Basic Acetate or Benzoate Method." For the separation of iron and titanium reference works on quantitative analysis, especially on iron and steel, should be consulted.

Determination of Calcium Oxide. After the removal of iron, aluminum, etc., the calcium is precipitated as the oxalate by slowly neutralizing the solution containing an excess of oxalate ion with ammonia. If much magnesium is present, some of it will be carried down by the precipitate, due mostly to post-precipitation. An oxalate free from magnesium may be obtained by a second precipitation. The precipitate is ignited and weighed as calcium carbonate or as calcium oxide, the former method giving more accurate results.

Procedure. Acidify the filtrate from the ammonia precipitation slightly with hydrochloric acid, and concentrate it to 200 ml. For every gram of limestone, add to the boiling hot solution, slowly and with constant stirring, a solution of 1.5 g. of crystallized oxalic acid, $H_2C_2O_4 \cdot 2H_2O$, or 1.7 g. of ammonium oxalate, $(NH_4)_2C_2O_4 \cdot H_2O$, in 25 ml. of water. Filter this solution of the reagent if it is not perfectly clear. A portion of the calcium is usually precipitated, but most of it remains in solution. Add a few drops of methyl red or methyl orange as indicator. Add rapidly to the hot solution (conveniently from a buret) a filtered solution of dilute ammonia—5 ml. of the concentrated reagent to 50 ml. of water—until the precipitate first formed dissolves slowly *; then continue the addition drop by drop over a period of about 20 minutes until the solution is neutral or slightly alkaline. Add a little more of the oxalate to test for complete precipitation. Let the precipitate settle for one hour. If the ratio of magnesium oxide to calcium oxide is known to be small, the precipitate will be free from magnesium. In this case filter the precipitate through a filtering crucible if it is to be weighed as calcium carbonate (the better method), or through an ashless paper filter if it is to be weighed as calcium oxide. Wash the precipitate with cold, 1 per cent ammonium oxalate solution, ignite it under proper conditions as directed in the determination of calcium oxide in calcium carbonate, pp. 342-343, and weigh. If the amount of magnesium is unknown, or if it is known to be considerable, a second precipitation must be made. Decant as much as possible of the clear, supernatant liquid through a small (5.5 or 7 cm.) filter into a 600 or 800 ml. beaker, without disturbing the precipitate. Wash the filter 3 or 4 times with cold water. Add 50 ml. of concentrated nitric acid to the filtrate containing most of the magnesium, and place it on the hot plate to evaporate. Place under the funnel the beaker containing the main portion of precipitate and let boiling, dilute hydrochloric acid—5 ml. of the concentrated acid diluted to 20 ml.—drip around the edge of the filter to dissolve the small amount of calcium oxalate on the paper. Wash the filter several times with hot, 1 per cent hydrochloric acid. If the precipitate in the beaker has not already dissolved, apply heat for a few minutes. It may be necessary to add 1 ml. more of concentrated hydrochloric acid to obtain a clear solution. Dilute to 250 ml., add 0.5 g. of oxalic acid or ammonium oxalate, dissolved in a little water, heat the solution to boiling, and precipitate the calcium oxalate as before by the slow addition of dilute ammonia. Let the precipitate stand one hour, and then proceed as directed

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* The temporary formation of the precipitate and its slow disappearance upon stirring the solution serve to indicate that the major portion of the free acid has been neutralized; after this point the ammonia should be added slowly as directed.

under the determination of calcium oxide in calcium carbonate. Filter the precipitate through a filtering crucible (or through a 9 cm. ashless paper filter if the precipitate is to be ignited to calcium oxide) wash it with 1 per cent ammonium oxalate solution, dry and ignite for two hours at 500° C. to calcium carbonate. After weighing the residue, moisten it with a drop or two of a saturated ammonium carbonate solution, dry it in the oven at 110-120° C., and weigh again. This treatment converts any traces of calcium oxide into calcium carbonate and must never be neglected. Add the filtrate from this second precipitation to that from the first, and evaporate the combined liquids as directed below in preparation for the determination of magnesium. Calculate the percentage of calcium oxide. If the residue is to be weighed as calcium oxide, carry out the ignition as directed in the determination of calcium oxide in calcium carbonate, p. 343.

If duplicate determinations do not agree within 0.2 to 0.3 per cent of the weight of the sample, the difficulty may be due to an incomplete separation of the calcium from the magnesium. Either the calcium carbonate or calcium oxide may be dissolved in hydrochloric acid and be precipitated again and ignited. The filtrate should be added to the previous filtrates for the determination of magnesium. A little more oxalate ion must be added to the solution before this last precipitation, otherwise precipitation will be incomplete. If the weight of the calcium precipitate is not appreciably changed by this procedure, the original precipitate must have been free from magnesium. It is a good plan to dissolve the calcium carbonate or the calcium oxide and to keep the solutions until the results are accepted.

Alternative Method for Determination of Calcium Oxide. After the removal of iron, aluminum, etc., the calcium is precipitated as the oxalate in the presence of an excess of ammonium oxalate by neutralizing most of the acid in the hot solution with ammonia, and then neutralizing the rest of the acid very slowly with urea, which decomposes to form ammonia and carbon dioxide.[1]

$$(1)\quad (NH_2)_2CO + H_2O = 2NH_3 + CO_2.$$

Large crystals of calcium oxalate are obtained from this very

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[1] F. L. Chan, Dissertation, University of Michigan, 1932.

slow precipitation and a better separation from magnesium results. In case the precipitate is contaminated with magnesium, a second precipitation must be made. This last step is seldom necessary if the following procedure is adopted, and a volume of 600 ml. is maintained when considerable magnesium is present.

Procedure. Urea Method. Exactly neutralize the filtrate from the "R_2O_3" precipitate, using methyl orange or methyl red as an indicator, and dilute the solution to 300 ml. in a 600 ml. beaker. Add 2.0 ml. of concentrated hydrochloric acid and a weight of ammonium oxalate, dissolved in 30 ml. of water containing 2.0 ml. of concentrated hydrochloric acid, equal approximately to twice that of the original sample. Heat to boiling and add to the solution, while stirring, 15 g. of urea. Keep the liquid boiling gently until it becomes neutral. This neutralization process requires from 30 to 60 minutes. Cool the solution, add to it 4 g. of ammonium oxalate dissolved in 80 ml. of water, and allow it to stand from 3 to 5 hours, no longer. On long standing the calcium oxalate is contaminated with magnesium. Collect the precipitate in a weighed porcelain filtering crucible and wash it with cold 0.1 per cent ammonium oxalate solution. Prepare the filtrate and washings for the determination of magnesium by proceeding to the operations described on p. 399. Place the crucible in the drying oven for 30 minutes or more, then heat it for 2 hours at 480-500° C. in an electric muffle and weigh the calcium carbonate. To insure the absence of any traces of calcium oxide, always moisten the precipitate with a few drops of a concentrated solution of ammonium carbonate, dry in the oven at 110-120° C. for one hour and weigh again. Calculate the percentage of calcium oxide.

If the calcium carbonate is dark in color, more satisfactory results will be obtained by igniting it to calcium oxide as directed in the section discussing the determination of calcium oxide in calcium carbonate.

As a rule a satisfactory separation from magnesium even in dolomite is accomplished by one precipitation with this urea method. However, if duplicate determinations do not agree closely (i.e., within 0.2-0.3 per cent of the sample weight), an incomplete separation from magnesium may be the cause. In such a case dissolve the precipitate of calcium carbonate in dilute hydrochloric acid in a 600 ml. beaker, rinse off the crucible, and pass dilute hydrochloric acid through it with the aid of the filter pump. Add the washings to the main solution and precipitate the calcium oxalate again as described above. Ignite and weigh as before.

The presence of any appreciable amount of magnesium in the calcium carbonate may be detected by taking advantage of the fact that magnesium carbonate, stable at 100° C., quickly dissociates into magnesium oxide by brief heating at 450-500° C. Heat the calcium carbonate, which has been weighed after the treatment with ammonium carbonate and drying at 110° C., for 15-30 minutes at 450-500° C. and again weigh. A loss in weight of more than a few tenths of a mg. indicates the presence of magnesium.

Determination of Magnesium Oxide. It has already been pointed out that the presence of oxalate ion and of large amounts of ammonium salts causes the results for magnesium, when precipitated as magnesium ammonium phosphate, to be high. This error may be avoided either by a double precipitation or by removal of the interfering salts. In the latter method any silica present is also removed. Oxalate and ammonium ions may be removed by ignition, a very inconvenient procedure in this case, or by oxidation in solution with nitric and hydrochloric acids, the oxalate ion forming carbon dioxide and water, and the ammonium salts principally nitrous oxide and water, with some nitrogen and perhaps nitric oxide. Since chloride ion is already present in considerable quantity, only nitric acid should be added before the solution is evaporated to dryness.

If oxalate ion is not removed, it must be remembered that its presence greatly delays the precipitation of magnesium, and that more of the phosphate is required to make it complete. The first precipitate should, therefore, stand overnight before filtering.

Procedure. To the combined filtrates and washings from the removal of the calcium, add 50 ml. of concentrated nitric acid as already directed, and evaporate carefully to dryness on the hot plate in a 600 or 800 ml. beaker. Glass hooks on the edge of the beaker will greatly hasten this process, but care should be taken that the reaction does not become too violent during the latter part of the evaporation. In case the beaker is left overnight, it should be placed on the low temperature hot plate. A rapid evaporation without boiling is most effective. Only a small residue of magnesium salts should remain if the operation has been successful. If there is a large residue of salts, add 25-30 ml. of water, 50 ml. of concentrated nitric acid, 15 ml. of concentrated hydrochloric acid, and repeat the evaporation; keep the material as hot as possible without causing it to spatter. If silica was dehydrated with perchloric acid and ammonium salts were not completely removed by this process, the ammonium perchlorate in the dry residue, if heated sufficiently, will decompose rapidly but quietly, forming free chlorine, the process being accompanied by the production of light. This seems to do no harm, although mechanical loss may occur if the reaction is too vigorous. Moisten the residue with 2-3 ml. of concentrated hydrochloric acid and 20 ml. of water, warm the mixture for a few minutes until everything is dissolved except a little silica resulting from the action of the various solutions on the glass vessel. Filter into a 250 ml. beaker (preferably unscratched), wash the residue, and add to the filtrate 5-8 ml. of concentrated hydrochloric acid.[1] Dilute the solution to 125-150 ml., add 1.5 g. of diammonium hydrogen phosphate dissolved in a little water, cool the liquid to room temperature or below, and, while stirring constantly, add filtered, concentrated ammonium hydroxide very slowly until the solution is alkaline to methyl red. Stir the solution for a few minutes and add 5-10 ml. more of the ammonium hydroxide. Stir a few minutes longer and allow the cold solution to stand at least 4 hours, or preferably overnight. Filter through a Gooch crucible, wash the precipitate with cold dilute ammonium hydroxide—one part of concentrated reagent ammonia to 19 parts of water—dry it in the oven or over a very low flame and ignite at 1000-1100° C. to constant weight. Weigh as magnesium pyrophosphate, $Mg_2P_2O_7$, and calculate the percentage of magnesium oxide. A paper filter may be used if preferred; care should be taken to burn off the carbon slowly at a low temperature before the final ignition. See p. 333.

If, instead of removing oxalate and ammonium salts as directed above, it is desired to make a double precipitation, the first precipitate, after standing overnight, is dissolved and repre-

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[1] This is essentially the method of Hoffman and Lundell, J. Research Natl. Bur. Standards, 5, 279 (1930).

cipitated as directed under "Determination of Magnesium Oxide," p. 333. A second precipitation will, in any case, always give more accurate results and is advised if the time is available.

If the individual results do not agree closely, the difficulty may be due to a poor separation from calcium. The precipitate may be tested for calcium as follows: Dissolve it in hydrochloric acid, add ammonium hydroxide until a precipitate appears, and then add just enough acetic acid to dissolve the precipitate. Filter the solution if a slight flocculent precipitate remains. Heat the solution and add about 1 g. of ammonium oxalate dissolved in a little water. Calcium oxalate is practically insoluble in dilute acetic acid. If a precipitate forms, it should be granular in appearance and should not adhere to the glass. Otherwise it may consist of magnesium oxalate. (Why could not the calcium be precipitated in neutral or alkaline solution?)

The sum of the various determinations may be close to 100 per cent or it may be considerably less, depending on what other elements are present.

The amounts of silica and "R_2O_3" or combined oxides being known, the value obtained for the loss on ignition should be compared with that calculated from the percentages of calcium oxide and magnesium oxide found. Thus, since the loss on ignition is nearly all carbon dioxide, any large errors may often be detected if all of the calcium and magnesium were present as carbonates.

It sometimes happens that the determination of magnesium is ruined, and it is desirable in a second analysis to shorten the time required for the preceding separations. The following procedure is satisfactory: Give the sample a preliminary ignition of 30 minutes, and dissolve it in hydrochloric acid in a 400 ml. beaker. Dilute the solution to 200 ml., and boil for 5 or 10 minutes to remove *all* carbon dioxide. This last step is very important. Add a few drops of thymolphthalein indicator and then freshly prepared sodium hydroxide solution until the indicator turns blue ($p\text{H} = 10.5$). Boil for a moment, let the mixture settle, and filter off the precipitate which consists of magnesium hydroxide, "R_2O_3," silica, and a little calcium carbonate. Calcium hydroxide does not precipitate to any appreciable extent at this pH. Wash the residue with hot water, dissolve it in hydrochloric acid, and precipitate the calcium as calcium oxalate in the usual way. If considerable precipitate is formed, a second precipitation should be made. Remove ammonium salts in the filtrate as just directed. This evaporation to dryness also serves to remove whatever silica remains. To the clear solution add 1 g. of ammonium tartrate to prevent the precipitation of "R_2O_3," precipitate the magnesium ammonium phosphate in the usual way, and ignite it to the pyrophosphate.

Determination of Carbon Dioxide in a Carbonate. Samples of the carbonate are treated with hydrochloric acid in a special apparatus and the carbon dioxide evolved, after being freed from impurities and dried, is absorbed by a suitable reagent contained in an absorption bulb. The increase in weight of the bulb is a measure of the carbon dioxide in the sample. This determination introduces a new form of technique, the quantitative handling of a gas, and care must be given to each detail in the procedure if accurate results are to be obtained.

Construction of the Apparatus. The success of the determination depends largely upon the construction of a compact, gas-tight train. A suitable form of apparatus is shown in Fig. 55. *A* is a wide-mouth decomposition flask, which is supported on a wire gauze on a tripod or ring stand. The flask is closed with a two-hole rubber stopper, through which pass a small condenser *C* and a separatory funnel *B*. The upper end of the separatory

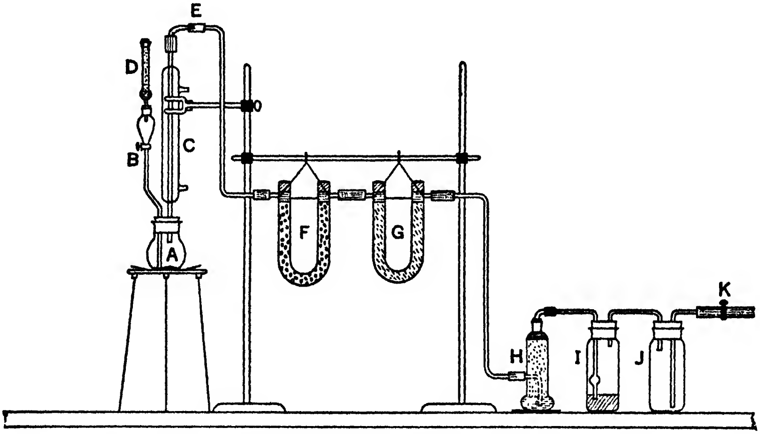

FIG. 55. Absorption Train for CO_2 Determination.

funnel is fitted with a one-hole rubber stopper containing a 150 mm. calcium chloride tube *D* filled with "ascarite" (sodium hydroxide-asbestos absorbent). A small plug of cotton prevents any ascarite from entering the separatory funnel. The upper end of the tube *D* is fitted with another plug of cotton and closed with a perforated cork. The condenser *C* is connected with the remainder of the train by an adapter *E* made by drawing out a large glass tube and bending it at right angles. The adapter is connected to the condenser with gum rubber tubing. The best quality of gum tubing should be used in making all connections and the glass joints should always be in contact with each other. The rubber connections may be wired as an added precaution against leakage. Ordinary 6 mm. glass tubing is used to connect the adapter to the 150 mm. U-tube *F*. The two tubes *F* and *G* are suspended with copper wire from a piece of heavy glass or iron rod, supported by ring stands, one of which may be used conveniently as a support for the condenser. The first U-tube serves to absorb water vapor that escapes from the condenser as well as to remove any hydrochloric acid or hydrogen sulfide from the gas.

The first third of tube *F* is filled with anhydrous copper sulfate which serves to remove any hydrogen sulfide, and the last two thirds with dehydrite, $Mg(ClO_4)_2$, or drierite, $CaSO_4 \cdot \frac{1}{2}H_2O$, both of which are efficient absorbents for water. If hydrogen sulfide is known to be absent, the copper sulfate may be omitted. The evolution of hydrogen sulfide may be prevented by adding chromic acid to decompose the carbonate, followed if necessary by sulfuric or perchloric acid. Anhydrous calcium chloride may be substituted for dehydrite or drierite, but it has certain disadvantages. It is not so efficient a drying agent and it must first be saturated with carbon dioxide to remove the calcium oxide which is usually present in it. The carbon dioxide must then be removed by passing air free from carbon dioxide through the tube. The ends of the tube are closed by inserting well fitting corks which should extend nearly to the outlets. The corks are rendered gas-tight by cutting them off flush with the tops of the U-tubes and covering the ends with sealing wax. The second U-tube is filled with drying agent, except for a space of about 2 cm. in length at the top, which is loosely filled with cotton. The ends of the tube are sealed in the manner described above. The U-tubes are joined to each other and to the tubes at either end with gum rubber tubing wired in place. From the second U-tube, a suitably shaped glass tube leads to the special absorption bulb *H* which is filled with fresh ascarite on top of which is placed a layer of drying agent 1 cm. thick. Spaces 1 cm. high at the top and bottom of the bulb are filled with cotton. The bulb shown in Fig. 55 is a very simple and inexpensive type. A better type is provided with stopcocks at each end, and contains a separate compartment for the drying agent, following the ascarite, to remove all water formed in the reaction between sodium hydroxide and carbon dioxide, instead of relying upon the drying power of ascarite. The Wesson bulb is a good example of this type.

The absorption bulb, as well as a similar absorption bulb which is placed beside it and is used only as a tare in making weighings, should rest on clean paper and not directly on the desk top. From the absorption bulb a tube leads to the bottle *I* containing concentrated sulfuric acid. This bottle serves both to indicate the rapidity of the gas flow through the train and to prevent any water vapor from entering the train from the aspirator end. The tube should dip into the acid to a depth of only a few millimeters. It is advisable for this tube to be enlarged at some point intc a bulb so that acid can not be sucked back into the absorption bulb if the suction is suddenly interrupted. If the tube that dips into the acid in *I* has no safety bulb, a bottle with tubes arranged like those in *J* should be inserted between *H* and *I*. The last vessel in the train is the empty bottle *J*, which acts as a trap to catch any water that might be drawn back from the aspirator. These two bottles should be closed with well-fitted rubber stoppers. The bottle *J* is connected to the aspirator pump by heavy walled tubing. A clamp *K* serves to regulate the gas flow.

Testing the Train. Before proceeding to an actual determination, the finished train must be tested for any possible leakage. This may be done by the following steps: 1. Tightly close the top of the ascarite tube on the separatory funnel with a rubber stopper; 2. Close the clamp *K* and turn on a gentle stream of water in the aspirator pump; 3. Slowly open clamp *K* until about one bubble per second passes through the indicator bottle; 4. Observe whether the rate at which gas bubbles through the indicator bottle rapidly slackens and finally comes to a stop, or at least decreases to one bubble in several minutes. If the bubbles continue to pass through the indicator bottle under these conditions, the apparatus must be examined systematically for the source of the leakage, and after the necessary changes have been made must be tested again to ascertain if the train is now free from leaks.

Another method of testing a train of this kind is to determine the carbon dioxide in a pure substance or one of known value, as described later, and to compare the value obtained with that which should be found.

Procedure. After the train has been found to be gas-tight, aspirate a current of air through the apparatus at the rate of about two bubbles per second for a period of ten minutes. Then stop the air current and take the absorption bulb to the balance case together with the tare absorption bulb. If the bulb is not provided with stopcocks, the ends should be closed by plugs made from short lengths of rubber tubing and glass rods. Handle the bulbs with filter paper or a clean cloth. After they have stood in the balance case for thirty minutes and are ready to be weighed, open the stopcocks of both bulbs for a moment or remove the plugs from the bulbs. Weigh the absorption bulb by placing it on the left pan of the balance and the tare bulb on the right pan along with the weights. This method of weighing is employed to eliminate the errors arising from the different quantities of moisture retained by large glass surfaces under varying atmospheric conditions, and from the varying density of the air. Return the bulb to the train and repeat the above procedure. The second weight of the bulb should agree with the first within 0.0005 g. If it does not, repeat this process until two successive weighings agree. As soon as constant weight is reached, weigh a 1 gram sample of the carbonate rock into the decomposition flask. Add 25-30 ml. of water to the sample and a few small pieces of porous porcelain to prevent bumping, and connect the flask to the train. Place 50 ml. of dilute hydrochloric acid—one part of the concentrated acid to one part of water—in the separatory funnel and replace the guard tube at the top of the funnel. Start the flow of water in the condenser. At the beginning disconnect the tube to the aspirator. Then admit the acid slowly into the decomposition flask, regulating the rate so that not more than two or three bubbles of gas per second pass through the indicator bottle. As soon as all the hydrochloric acid has been added and the rate of gas flow slackens, heat the flask with a small flame until the sample has dissolved. Without removing the flame from under the decomposition flask, connect the aspirator; take care first to close the clamp *K* and then to open it gradually until the flow of bubbles reaches two or three a second. Boil the solution in the decomposition flask gently for two or three minutes. On removing the flame open the stopcock in the separatory funnel to prevent any back pressure due to condensation of steam; at the same time regulate the aspirator clamp so as to maintain a constant flow of gas. Continue to draw air through the train for 30 minutes, and increase the rate of gas flow slightly toward the end of this period. Reweigh the absorption bulb in the same manner as before. The increase in weight represents the carbon dioxide in the sample.

The determination is repeated until two results are obtained that agree within 0.3 per cent. The weight of the absorption bulb after the first determination may be used as the starting point for another determination without repeating the initial process of obtaining constant weight. It is advisable, however, to reweigh the bulb if it is not used on the same day. When not in use the absorption bulbs should be closed and the train completely assembled to prevent the entrance of carbon dioxide into the apparatus.

THE ANALYSIS OF AN INSOLUBLE SILICATE[1]

Principle. The silicate is rendered soluble by fusing it with sodium carbonate in a platinum crucible. The soluble silicate is dissolved in dilute hydrochloric acid and the solution is evaporated to dryness to dehydrate the silica. The dry residue is treated with concentrated hydrochloric acid to dissolve oxides and basic salts and the silica is filtered off. A second recovery of silica is made and the two precipitates are ignited in a platinum crucible and weighed. The silica is then volatilized as silicon tetrafluoride by treatment with hydrofluoric and sulfuric

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[1] Hillebrand and Lundell, Applied Inorganic Analysis, John Wiley & Sons (1929), p. 645; Washington, Analysis of Rocks, John Wiley & Sons (1930), 4th edition, p. 148.

acids. The excess of acid is evaporated and the residue ignited to the oxides. The loss in weight of the precipitate represents pure silica.

In the filtrate from the silica, metals of the acid hydrogen sulfide group, if present, are removed as sulfides; then iron, aluminum, and titanium are precipitated by the ammonia or basic benzoate or succinate method, and finally calcium and magnesium are determined. If zinc is present it is separated, before the calcium and magnesium, as sulfide in a solution of *p*H 2-3. Manganese, if desired, may be precipitated with the iron, etc., by adding with the ammonia an oxidizing agent such as bromine, hydrogen peroxide, or a persulfate. Otherwise it may be separated from calcium and magnesium by precipitation as the sulfide or as the hydrated dioxide. Alkali metals must be determined on a separate sample which is decomposed by fusion with a mixture of calcium carbonate and ammonium chloride. This method will not be described here.

Many of the sources of error in the analysis of an insoluble silicate have been described in the preceding pages under the "Determination of Silica in a Soluble Silicate," p. 355 and "Analysis of Limestone," p. 389.

Procedure for Silica. Weigh into a 20-30 ml. platinum crucible 0.7-0.8 g. of the finely powdered, dried silicate, add 5 times its weight of anhydrous sodium carbonate, and mix the two solids thoroughly by stirring with a rounded glass rod or a spatula. Cover the mixture with a little more of the carbonate. Cover the crucible, heat it, supported in a nichrome triangle, until the bottom of the crucible is a dull red, and after five minutes gradually increase the heat to the full capacity of a burner of the Meker type. Maintain this temperature until a quiet, liquid fusion is obtained; lift the cover of the crucible occasionally to examine the contents. This part of the operation should require 20-30 minutes. Be sure that all material on the cover and sides is completely fused. The fused mass will not usually be perfectly clear. Remove the flame and tilt the crucible as it cools in order to increase the surface of the contents. When cool, tap the inverted crucible gently on the bottom of a 300 ml. casserole. The cake will usually fall out and the small amount of solid adhering to the crucible and cover is dissolved in water and added to the main solution. Add to the covered casserole a mixture of 100 ml. of water and 25 ml. of concentrated hydrochloric acid. If the cake is not readily removed from the crucible, put the latter into the casserole and add the acid as directed. In this case add a few drops of alcohol if the cake is green from the presence of a manganate. The alcohol prevents the liberation of chlorine which might attack the crucible. Keep the solution warm until the mass has disintegrated and the crucible can be removed and washed clean.

Evaporate the solution to dryness on a low temperature hot plate. Moisten the residue with 5 ml. of concentrated hydrochloric acid and 5 ml. of water, and evaporate again to dryness. Keep the dry residue at a temperature of 100-110° C. for at least one hour, or overnight if more convenient. Add to the residue 5 ml. of concentrated hydrochloric acid to dissolve the oxides and basic salts, and stir up the pasty mass. As soon as these oxides have dissolved, add a little water from a wash bottle and continue stirring. Then add about 100 ml. of water, heat the solution just to boiling, filter off the silica and wash it 5 or 6 times with warm, dilute hydrochloric acid—one part of the concentrated acid to 10 parts of water. Wash finally 4 or 5 times with water, or until chloride ion is removed. Evaporate the filtrate to dryness and proceed as before to recover the small amount of silica which has remained in solution. Filter through a separate filter. Transfer the two precipitates to a platinum crucible, burn off the filter carefully, add a drop of concentrated sulfuric acid, evaporate to dryness and heat the covered crucible to the full heat of a burner of the Meker type for 30 minutes. Cool and weigh the crucible and contents. Repeat the ignition for 15 minute periods until the weight is constant. This silica is impure. Moisten it with water, add two drops of concentrated sulfuric acid and about 5 ml. of hydrofluoric acid. Judge this amount by the depth to which the crucible is filled. If any hydrofluoric acid is spilled on the hands it must immediately be washed off with ammonia water, for otherwise painful ulcers may result. Evaporate the acid slowly under a hood with special care to avoid spattering, heat the crucible to a bright red heat for 15 minutes to convert the sulfates into the oxides, and weigh the residue. The loss in weight is the weight of pure silica. For the reactions involved, see p. 359.

The reasons for the various steps in this process are discussed in Chapter XVI in the section on "The Determination of Silica in a Soluble Silicate."

Separation of the Metals. The combined filtrates from the silica contain the chlorides of iron, aluminum, titanium, manganese, calcium, magnesium, and possibly other metals. The combined oxides of the first four, sometimes called "R_2O_3," are determined by two precipitations with ammonia (in the presence of persulfate ion, bromine, or other oxidizing agent if manganese is present). The procedure is essentially that described in the analysis of limestone, except that the precipitate in this case will be very much larger, and must be ignited at 1000° C. or higher. The solution should be barely alkaline to methyl red (pH or 6.5). If the pH is 8 or more, the precipitation of aluminum hydroxide will be incomplete. If a separation from manganese is desired, the pH must not be above 6.5. The iron in the precipitate may be determined volumetrically and the aluminum obtained by difference if no other oxide is present.

The determination of calcium and magnesium is carried out as in limestone, using two precipitations of each, except that the amounts present here will be much smaller and therefore the volumes of solutions used and weights of reagents added should be reduced.

Review Questions and Problems

1. Outline a method for the complete analysis of a carbonate of ferrous iron, manganese, lead and calcium (five determinations).

2. Outline a method for the complete analysis of an insoluble silicate containing barium, magnesium, aluminum, cadmium.

3. How does the method of determining calcium and magnesium in a mixture of their phosphates differ from that ordinarily used?

4. In a sample of dolomitic limestone containing 5.00 per cent of silica, 3.50 per cent of combined oxides and showing 43.00 per cent loss on ignition, what is the percentage of calcium oxide and of magnesium oxide, assuming that the loss is due entirely to carbon dioxide from the carbonates of calcium and magnesium?

5. A 0.7000 g. sample of a mixture of carbon, calcium carbonate and inert material was treated with acid and the ascarite absorption bulb gained 0.1407 g. A second sample weighing 0.6000 g. was burned in oxygen at 900° C. and yielded 0.2306 g. of carbon dioxide. Calculate the percentage of carbon dioxide and of free carbon in the sample.

Ans. 5.00 per cent carbon and 20.10 per cent carbon dioxide.

6. From a sample of limestone weighing 1.1300 g., 0.0510 g. of Mn_3O_4

and 0.3150 g. of magnesium pyrophosphate were obtained. Calculate the percentage of manganous oxide and of magnesium oxide in the sample.

7. How much urea, $CO(NH_2)_2$, is required to neutralize by its hydrolysis the acid in 10.00 ml. of 35.00 per cent hydrochloric acid, sp. gr. 1.18?

8. What error in the per cent of magnesium oxide will be caused by the presence of 2.00 per cent of calcium oxide included as $Ca_3(PO_4)_2$ in the precipitate of magnesium pyrophosphate?

Ans. 1.34 per cent.

9. In the analysis of a sample of limestone weighing 1.0550 g., the weight of impure silica was 0.0510 g. After treatment with hydrofluoric and sulfuric acids a residue of 0.0025 g. of the oxides of aluminum and iron was obtained. In the determination of combined oxides the weight of precipitate was 0.0410, from which 0.0015 g. of silica was recovered. Calculate the percentages of silica and of combined oxides in the sample.

10. How much 70.00 per cent perchloric acid, sp. gr. 1.674, is required to neutralize 10.0000 g. of calcium carbonate?

11. Suggest an alkalimetric method for the titration of magnesium in the presence of calcium. Excess of hydrochloric acid is present. Magnesium hydroxide precipitates at a *p*H of 10.5. Would ferric and aluminum salts interfere?

12. In the volumetric determination of calcium what error will be caused by the presence of 1.50 per cent of magnesium oxide in the form of magnesium oxalate?

13. In a sample weighing 1.0550 g. the magnesium is precipitated as magnesium ammonium arsenate, which is dissolved in hydrochloric acid. After the addition of potassium iodide, the iodine is titrated with 0.1230 *N* thiosulfate, of which 40.10 ml. is required. Calculate the percentage of magnesium oxide in the sample.

14. A mixture containing only calcium oxide and magnesium oxide and weighing 0.8632 g. is converted into the mixed sulfates weighing 2.2642 g. Calculate the percentage of each oxide present.

Ans. 35.03 per cent MgO; 64.97 per cent CaO.

CHAPTER XIX

THEORY OF ELECTROLYTIC PRECIPITATIONS AND SEPARATIONS

Most of the methods of gravimetric analysis depend upon the precipitation of the ion that is to be determined, by the addition of a suitable reagent. The direct electric current may also be used as a precipitating agent. The amount of one substance that is present in a solution is determined by finding the gain in weight of a suitable electrode, previously weighed, after the deposition of the substance in question has been completed. The positive electrode, or anode, is usually of platinum or one of its alloys like platinum-iridium. The negative electrode, or cathode, may be of platinum or of a less expensive metal like tantalum, gold, silver, mercury, or copper. The process of electrolytic determination is called electroanalysis. In this way copper, silver, gold, mercury, cadmium, nickel, cobalt, zinc, antimony and tin, and, less commonly, other metals may be determined at the cathode. Chlorine, bromine and iodine may be liberated and deposited upon a silver anode. Lead and manganese are deposited as the higher oxides, PbO_2 or MnO_2, at the anode under suitable conditions. The determination of copper at the cathode and of lead peroxide at the anode are the determinations most frequently used in general analytical practice.

Apparatus for Electrolysis. A diagram of apparatus for electroanalysis is shown in Fig. 56. The source of direct current may be a series of lead or other storage batteries, a dynamo, or rectified alternating current (electrolytic, thermionic, or oxide-metal rectifier). The electrode upon which the deposition takes place may be either a dish, cylinder, cone, or gauze of suitable material; the Winkler gauze form has the greatest ratio of area to weight, and is a very satisfactory device. In some cases it is desirable to use a mercury cathode. This may be prepared by partially filling with mercury a weighing bottle into which a platinum wire is sealed near the bottom.

Electrical Units. The following definitions of units should be recalled: the *coulomb,* or unit quantity of electricity, is that quantity which is associated with or will deposit 0.001118 g. of silver. Electricity in motion is called current. The unit of current is the *ampere* and is equal to a rate of flow of one coulomb per second. One ampere, flowing for one second will deposit, therefore, 0.001118 g. of silver. An *ampere-hour* is a current of one ampere operating for one hour; it will deposit 0.001118 × 60 × 60 or 4.0248 g. of silver. The *ohm* is the unit of resistance, and is the resistance offered to a current by a column of mercury 106.3 cm. long and of uniform cross section, and weighing 14.4521 g. at 0° C. The *volt* is the unit of electromotive force (E.M.F.), and is the E.M.F. which causes a current of one ampere to flow through one ohm of resistance. The *volt-coulomb* is the unit of electrical energy, and is usually called the *joule.* The *watt* is the unit of power and equals 1 joule per second. The product, *volts* × *amperes,* is equal to *watts.* For example, if a lamp on a 110 volt circuit uses 40 watts, then the current flowing is: 110 × amperes = 40; amp. = 0.3636.

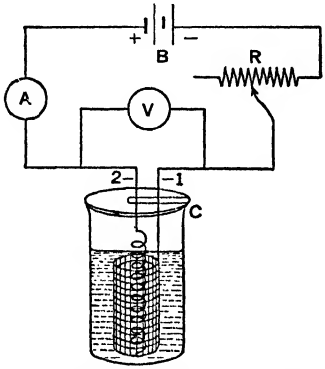


FIG. 56. Apparatus for Electroanalysis. *A,* Ammeter; *B,* source of direct current; *R,* a variable resistance; *V,* Voltmeter; 1, Winkler gauze electrode (may be of platinum or other material); 2, spiral anode of platinum or platinum-iridium; *C,* split, perforated or slotted watch glass.

Laws of Electrolysis. Ohm's law states the relation between current, resistance and potential, or E.M.F. It is usually expressed in the form

$$\text{Current strength} = \frac{\text{electromotive force}}{\text{resistance}}, \text{ or } I = \frac{E}{R}$$

if the current strength, I, is expressed in amperes, the electromotive force, E, in volts, and the resistance, R, in ohms. This law applies to all conductors, including electrolytes.

The relations between the quantity of electricity passed through an electrolyte and the electrochemical changes taking place at the electrodes are expressed in two laws known as Faraday's laws of electrolysis. The laws are:

1. *The quantity of a given substance which is liberated at an electrode is proportional to the quantity of electricity passed through the system.* Thus, for example, 1 coulomb deposits 0.001118 g. of silver, 2 coulombs deposit 0.002236 g. of silver, etc.

2. *The amounts of different substances which are deposited by the same quantity of electricity are proportional to the chemical equivalents of the substance.* The second law implies that a given quantity of electricity when passed in series through solutions of silver, cupric copper, and cadmium, for example, will deposit amounts of the metals that stand in the ratio:

$$\text{silver} : \text{copper} : \text{cadmium} \text{ as } 107.88 : \frac{63.57}{2} : \frac{112.41}{2}.$$

If the electrolysis consists in the solution of silver at a silver anode in contact with silver nitrate, and deposition of silver at the cathode, equal amounts of the metal dissolve and deposit respectively. Similarly a given quantity of electricity passed in series through chloride, bromide, and iodide solutions will liberate amounts of chlorine, bromine, and iodine which stand in the ratio: 35.457 : 79.916 : 126.92, provided the sole anode process is the liberation of halogen in each case. If two ions are discharged simultaneously, as, for example, oxygen and chlorine, by a quantity of electricity sufficient to discharge one gram equivalent of a single substance, then a portion x of an equivalent of oxygen and a portion y of an equivalent of chlorine will be discharged, but the sum, $x + y$, will equal 1 equivalent.

The fundamental quantity of electricity, which is implied in Faraday's second law, for the transfer of a gram equivalent of a substance from electrode to solution, or vice versa, is equal to 96,500 coulombs, and is called the *faraday*. One faraday, F, is able to liberate 107.88 g. of silver, 35.457 g. of chlorine, $\frac{63.57}{2}$ g. of cupric copper, etc.

The Factors Which Affect Electrodepositions. Water itself dissociates into hydrogen and hydroxyl ions according to the equation $H_2O \rightleftharpoons H^+ + OH^-$. The deposition of a metal at the cathode, therefore, involves a separation of the ions of the metal from hydrogen ions if an aqueous solution is electrolyzed. Similarly the anode process may involve a separation of certain anions from hydroxyl ions. In those cases where hydrogen is deposited simultaneously with the metal if the hydrogen is liberated rapidly enough to cause bubble formation at the cathode in the early stages of the deposition of a metal, the latter may form in a spongy, poorly adherent form that is apt to oxidize when dried or to contain impurities. The conditions are regulated to avoid the foregoing difficulties as far as possible. The important factors that need to be controlled are: The voltage applied at the electrodes, the amount of current per unit area of electrode or the current density, as this factor is termed, the *p*H of the solution and the temperature of the solution. Mechanical stirring and the use of substances containing complex rather than simple ions are other factors that are important. In order better to understand this rather complex subject of electroanalysis it is well to consider somewhat in detail such topics as cells, electrode potential, polarization, decomposition potential and over-voltage.

Voltaic and Electrolytic Cells. A cell may be defined as an arrangement of two electrodes and one or more solutions of electrolytes in a suitable container. If the arrangement is capable of furnishing electrical energy to some external system it is called a *voltaic cell.* The chemical energy of the reaction within the cell is converted more or less completely into electrical energy; some of the chemical energy may be converted into heat or other forms of energy. If, on the other hand, electrical energy is supplied from some external source and causes a current of electricity to flow through the cell the arrangement is called an *electrolytic cell.* The electrical energy from the external source is converted into chemical energy within the cell. The changes at the electrodes are completely accounted for by Faraday's laws of electrolysis.

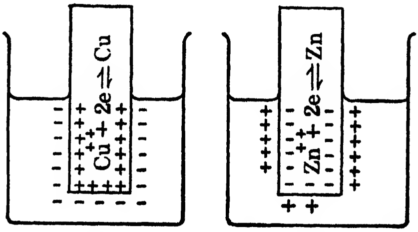
Frequently the same arrangement of electrodes and solution may function at one time as a voltaic cell and at another as an electrolytic cell. The lead storage cell, or accumulator, is the most familiar illustration. When the battery is used to furnish current, as in starting the motor of an automobile, the reaction that follows proceeds from left to right:

$$PbO_2 + 2H_2SO_4 + Pb \rightleftharpoons 2PbSO_4 + 2H_2O.$$

When the battery is being charged the reaction is reversed and lead peroxide is formed at the anode and lead at the cathode. A similar situation is built up as soon as an electroanalysis has begun to yield products of electrolysis at the anode and cathode. If, after electrolysis has continued for some time, the external source of current is disconnected it is found that the cell is now a voltaic one capable of furnishing current; it is obvious that the potential applied from the external source must be greater than that of the voltaic cell thus produced, if a current is to be forced continuously through the electrolytic cell, since the voltaic cell that is formed tends to oppose the flow of the current by which it is produced.

Single Electrode Potentials and the Electromotive Force Series. When any solid or liquid chemical element that is a conductor is placed in contact with a solution of its ions a potential is developed at the interface between the element and the solution. If the element is a gas, the potential between element and ion may be observed with the aid of a strip of unattacked metal, e.g., Pt, Au, etc. The magnitude of the potential appears to depend upon the relative tendencies of the ions of the element to leave the electrode and the opposing tendency, which is proportional to the osmotic pressure and hence to the concentrations of the ions of the element in the solution. Depending upon the nature of the element and the concentration of its ions, the potential at the interface may be positive, zero or negative. A copper rod dipping into a solution of copper sulfate (M) appears to have a double layer such that the copper rod is positive relative to the solution as indicated in *a*, Fig. 57. The deposited copper ions form the positive layer and an equivalent amount of sulfate ions form the negative part of the double layer. In *b*, Fig. 57, is illustrated a double layer in which the rod of metal is negative; this is due to the relatively great tendency of ions of active metals, e.g., Zn, Mg, etc., to enter the ionic state. In this case the negative layer consists presumably of excess of electrons remaining when the layer of zinc ions splits off to form the positive part of the double layer. This double layer constitutes the *electrode potential.*

Aside from relatively minor factors such as condition of strain or crystal form of the electrode material, temperature and pressure effects, etc., the major factors that determine the magnitude of an electrode potential relative to that of another electrode are: *First,* the tendency of the element to furnish ions (electrolytic solution pressure). At a given temperature and pressure this is a characteristic constant of any stable form of the element. *Second,* the osmotic pressure of the ions, which depends only upon their concentration, at constant temperature. The standard osmotic pressure that has been adopted is one that will make the activity of the ions equal to one. On this basis the elements may be arranged in a table according to their single electrode potentials. Such an arrangement of the elements is given in Table XX. The single electrode potentials under this special condition of unit ion activity is called the *standard electrode potential,* and is commonly represented by E_0. Since these potentials are all relative, any one may be selected for reference and given the value zero; the normal hydrogen electrode is the one generally so selected. Since the electrolytic solution pressure and therefore the normal electrode potential depends upon the temperature, it is necessary to specify the temperature.



(*a*) (*b*)

FIG. 57. Electrolyte double layers. (*a*) Copper in contact with a solution molar in cupric sulfate. (*b*) Zinc in contact with molar zinc sulfate.

The Influence of Concentration on Electrode Potential and Concentration Polarization. A voltaic cell is merely a combination of any two electrodes together with the appropriate solutions. One of the most familiar voltaic cells is the Daniel cell: $\mathrm{Cu} \mid (M)\mathrm{CuSO_4} \parallel (M)\mathrm{ZnSO_4} \mid \mathrm{Zn}$.

If the ion concentration, or more accurately, the ion activity is unity in both cases then each electrode will have its normal value or the one given in the table. The potential of the cell will be equal, therefore, to the difference between the two normal values of $E_{0cell} = E_{0Cu} - E_{0Zn}$. When such a cell is allowed to furnish electrical energy, copper ions will be deposited from the solution onto the electrode and zinc ions will go from the metal into the solution. The ion concentration in each case, and therefore the potential of the cell will be changed. Since the copper ion concentration will be reduced the potential will be more negative.

Suppose now this cell is connected to some source of potential greater than its own. In such a case current would be forced through the cell in the opposite direction. Copper ions would enter the solution from the electrode and increase their concentration and the potential of this electrode would become more positive. At the same time zinc ions would be removed from the solution and the electrode potential of the zinc would become more negative.

Such changes in electrode potential as just described are known as *concentration polarization.* It is evident that concentration polarization will always be present whenever current passes through a cell no matter whether it is functioning as a voltaic or electrolytic cell.

Chemical Polarization. There is another kind of polarization known as chemical polarization. If a certain small E.M.F. is applied to an electrolytic cell, only a very minute current passes, and no electrolysis occurs. If this potential is gradually increased there will be only a slight increase in the current, until at some point the current increases rapidly and electrolysis begins. This is shown in Fig. 58. That particular value, *a*, represented by the break in the current potential curve, is called the *decomposition potential.* The cell has been *chemically polarized* due to the changes produced by electrolysis. At lower potentials than this no visible action has taken place at the electrodes; above this value material is continuously set free at the electrodes. The decomposition voltages for normal solutions of all acids with relatively stable anions (sulfuric, nitric, phosphoric, perchloric, etc.) are all very close to 1.67 volts, as are also those of most bases, since in all of these cases the same process occurs: liberation of hydrogen at the cathode and oxygen at the anode. At the anode, $H_2O = 2H^+ + \frac{1}{2}O_2 + 2e$. At the cathode $2H^+ + 2e = H_2$. Sum: $H_2O = H_2 + \frac{1}{2}O_2$. When a salt is electrolyzed, the net result may be expressed in an equation such as:

$$Cu^{++} + 2NO_3^- + H_2O = Cu + \tfrac{1}{2}O_2 + 2H^+ + 2NO_3^-.$$

A portion of the oxygen that is liberated at the anode often appears in the form of ozone. For solutions of metallic salts, the decomposition voltage depends primarily upon the nature of the metal and little upon the nature of the anion, provided oxygen is the sole product liberated at the anode. For equivalent solutions of cadmium nitrate and cadmium sulfate, the values are respectively 1.98 and 2.03 volts; cadmium chloride, however, has a lower value, 1.88 volts, the anode process being different.

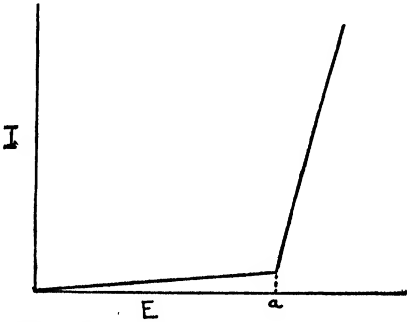


FIG. 58. Decomposition Potential. The discontinuity (a) of the current (I) plotted against applied voltage (E) marks the beginning of the separation of the products of electrolysis in substantial amounts.

It is evident from what has been said above that every ionic material requires a certain potential to cause it to discharge on the electrode. Theoretically this potential should be the same as the potential which an electrode of the material being deposited would show in the same solution. It usually happens, however, that the material does not start depositing at this theoretical value, but at a higher one. This difference in potential between the theoretical value at which an ion should be discharged and the potential at which it actually is discharged is called *overvoltage*. In the case of hydrogen the explanation commonly adopted is that a film of atomic hydrogen collects over the electrode surface. On a platinized platinum surface this does not occur because platinum black catalyzes the combination of atomic into molecular hydrogen.

Metals show small overvoltage effects in general. For the deposition of copper on a copper surface at low current densities the overvoltage is about 0.01 volt; for iron on an iron surface it may be as high as 0.1 to 0.14 volt. Oxygen shows an overvoltage of 0.4 volt at the anode in acid solution on smooth platinum, with current densities of 0.02 to 0.03 amp. per sq. cm.

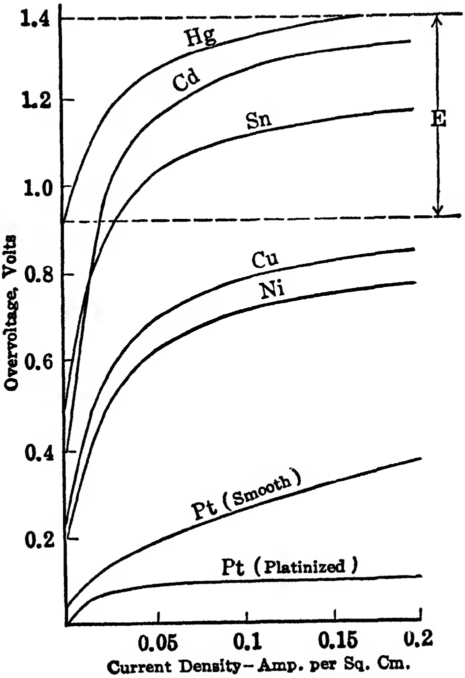


FIG. 59. Cathode Over-voltage of Hydrogen on Various Metal Electrodes. Plotted from data of Knobel, Caplan and Eiseman, Trans. Am. Electrochem. Soc. **43**, 55 (1923) and other sources.

Overvoltage depends upon several factors; one of the most important is the material being used as electrode. For instance, if the cathode is platinized platinum the break in the cathode current curve would come at a value which is the same as a hydrogen electrode would show in this solution; in other words hydrogen ions are discharged on a platinized platinum electrode at the theoretical potential. If any other material is used a greater potential than the theoretical must be applied before the hydrogen ions are discharged, and this difference is the overvoltage of hydrogen on this material.

Another important factor that affects overvoltage is *current density,* an increase in which always increases overvoltage. Current density is the current per unit area of electrode surface. It is usually expressed in amperes per sq. cm.; in electroanalysis a larger unit, amperes per square decimeter (100 sq. cm.) is often used. This larger unit is given the symbol N.D._{100}. Thus, $\text{N.D.}_{100} = 1.52$ means that 1.52 amperes are passing per 100 sq. cm. of electrode in contact with the solution.

Temperature always affects overvoltage. An increase in temperature decreases overvoltage. Ions of different materials are influenced to different degrees by the various factors affecting overvoltage.

Figure 59 represents the various cathode decomposition potentials for hydrogen on the different electrodes. In this set of curves the decomposition potential is the potential value at which the curve starts in each case. The overvoltage is given by the actual value on the potential scale in this case since the material being deposited is hydrogen and the zero on the potential axis is taken as the theoretical value for the hydrogen electrode in the solution used or it is the value at which hydrogen is actually deposited on the platinized electrode. For any given material the difference in the potential value at the point where the curve starts and the value at any given current density gives the overvoltage due to current density. Thus, E in Fig. 59 is the overvoltage for hydrogen deposition on mercury at a current density of 0.2 ampere per sq. cm.

The Voltage Applied to the Electrodes. The general relations between applied E.M.F. and the effects which it must overcome are summarized in the following scheme:

$$\text{E.M.F. applied, } E_{\text{appl.}} \geqq \left\{ \begin{array}{c} \text{Ohmic resist., } IR \\ + \\ \text{Back E.M.F. or} \\ \text{Decomposition Voltage, } E_d = \left\{ \begin{array}{c} \begin{array}{c} \text{Reversible} \\ \text{E.M.F., } E_r \end{array} = \Big\} E_{\text{anode}} - E_{\text{cath.}} \\ + \\ \text{Overvoltage, } \omega = \left\{ \begin{array}{l} \text{Effect at} \\ \text{anode } \omega_a - \\ \text{Effect at} \\ \text{cathode } \omega_c \end{array} \right. \end{array} \right. \end{array} \right.$$

Expressed more briefly in symbols:

$$E_{\text{appl.}} \gtreqless IR + E_d. \qquad E_r = E_a - E_c.$$
$$E_d = E_r + \omega. \qquad \omega = \omega_a - \omega_c.$$

Electrode Potential or Deposition Potential of an Ion as Influenced by Concentration of the Ion. As pointed out earlier, the potential of an electrode depends upon the difference between the electrolytic solution pressure of the material of the electrode and the osmotic pressure of the ions of the electrode material. The change in electrode potential with ion concentration is given by a formula originally proposed by Nernst. It has the form

$$E = \frac{2.303\,RT}{nF} \log \frac{C_1}{C_2},$$

where 2.303 is the constant for conversion of natural to common logarithms, R is the gas constant, T the absolute temperature, F the faraday, n the valence of the ion involved, C_1 and C_2 the two concentrations. Substituting the respective values in this equation

$$E = \frac{2.303 \times 1.985 \times 4.184 \times T}{n \times 96494} \log \frac{C_1}{C_2}$$
$$= \frac{0.0001982\,T}{n} \log \frac{C_1}{C_2}$$

and for 25° C.

$$E = \frac{0.0591}{n} \log \frac{C_1}{C_2}.$$

The product 1.985 calories (R) × 4.184 gives R in joules. 96494 coulombs is the value of F. If one of these concentrations or, more correctly, activities, is taken as unity and the corresponding E is called E_0, then the equation becomes at 25° C.:

$$E = E_0 + \frac{0.0591}{n} \log C.$$

Table XX gives the values for the standard electrode potentials of some common systems.

Table XX. Standard Electrode Potentials at 25° C.[1]

Electrode Reaction	E_0, Volts	Electrode Reaction	E_0, Volts
$Li^+ + e \rightleftharpoons Li$	−3.02	$H^+ + e \rightleftharpoons \frac{1}{2}H_2$	0.0000
$K^+ + e \rightleftharpoons K$	−2.922	$Cu^{++} + 2e \rightleftharpoons Cu$	0.3448
$Na^+ + e \rightleftharpoons Na$	−2.712	$\frac{1}{2}I_2 + e \rightleftharpoons I^-$	0.5355
$Zn^{++} + 2e \rightleftharpoons Zn$	−0.762	$Hg_2^{++} + 2e \rightleftharpoons 2Hg$	0.7986
$Fe^{++} + 2e \rightleftharpoons Fe$	−0.443	$Ag^+ + e \rightleftharpoons Ag$	0.7995
$Cd^{++} + 2e \rightleftharpoons Cd$	−0.402	$\frac{1}{2}Br_2 + e \rightleftharpoons Br^-$	1.0652
$Ni^{++} + 2e \rightleftharpoons Ni$	−0.250	$\frac{1}{2}Cl_2 + e \rightleftharpoons Cl^-$	1.3583
$Sn^{++} + 2e \rightleftharpoons Sn$	−0.136	$Au^{+++} + 3e \rightleftharpoons Au$	1.42
$Pb^{++} + 2e \rightleftharpoons Pb$	−0.126		

Electrolytic Separations and Completeness of Deposition. In connection with the possibility of the electrolytic determination of a given metal it is always necessary to take into consideration the other ions present and the overvoltage to be expected. Suppose for instance the solution is 0.01 *M* with respect to silver and 1 *M* with respect to copper. The potential at which silver would start to deposit from such a solution is given by the equation

$$E = E_0 + 0.0591 \log 10^{-2} = 0.800 - 0.118 = 0.682 \text{ volt}$$

When the silver ion has been reduced to a negligible value, say 10^{-7} *M*, the potential is

$$\begin{aligned} E &= 0.800 + 0.0591 \log 10^{-7} \\ &= 0.800 - 0.4137 = +\,0.386 \text{ volt.} \end{aligned}$$

From the table of standard potentials it is observed that the potential of the copper electrode in a 1 *M* solution is 0.344 which is even lower than the value of silver in the 10^{-7} *M* solution, which means that no copper would be deposited. In general it may be said that a univalent metal can be completely separated from another if the deposition potential of the other metal from that

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[1] The numerical values are selected from Oxidation Potentials, by W. M. Latimer, Copyright 1938 by Prentice-Hall, Inc. and reproduced with permission. The convention here used with regard to the sign of the E_0 values is the one officially adopted by most authorities. According to this convention the electrode potential is given the sign which the metal has toward the solution. Copper, for example, is positive toward a normal solution of copper sulfate.

solution is less by about 0.35 volt than the starting deposition potential of the first metal. In the case of the separation of a bivalent metal the difference may be only about 0.2 volt.

A type of electrolytic separation of great practical importance is the determination of a practically pure metal in a water or acid solution. From a consideration of the electromotive force table it might be expected that such separations would be limited to metals more positive than hydrogen; this, however, is by no means the case.

In most electrochemical processes overvoltage is something to be avoided as much as possible since it increases energy consumption. In electroseparations, however, it renders a very valuable service. It has already been pointed out that hydrogen starts to deposit at its theoretical value only on platinized platinum. For any other metal a more negative value is required. The magnitude of this negative value depends in a rather pronounced manner upon the metal used as cathode, the physical condition of the metal, the current density and the temperature. Another point to be remembered is the influence of hydrogen ion concentration on hydrogen deposition potential. Even on a platinized platinum electrode hydrogen would not start to deposit from a neutral water solution until the electrode had a value of $E = 0.0591 \log 10^{-7} = -0.4137$ volt. Then, if the metal to be separated was cadmium, the overvoltage for hydrogen deposition at very low current density is about 0.4 volt and for a current such as would be used it is more than one volt. This means that cadmium could be completely separated even from a fairly acid solution.

It is even possible to deposit sodium and potassium if a mercury cathode is used. Three factors contribute largely to this: (a) Fig. 59 shows that hydrogen on mercury has a very high overvoltage, (b) the hydrogen ion concentration may be made very low, (c) sodium and potassium dissolve in the mercury and thus are prevented from acting as massive metal, or in other words, the electrolytic solution tendency is held very low.

A convenient apparatus for following changes in electrode potentials during an electrolytic deposition is shown in Fig. 60. The battery Bat_1 furnishes current for the electrolysis through the circuit *Am* (ammeter) electrodes 1,2 and the left-hand resistance, *R*. In order to follow the changes at electrode 2, the

E.M.F. of the cell composed of electrode 2, the solution in the beaker and the auxiliary Hg-Hg_2SO_4-K_2SO_4 half-cell, 3, is measured. Since the latter half-cell has a constant value, the changes at electrode 2 may be found from the observed values of this cell by subtracting the value for the half-cell.

The measuring circuit, *A*, *Bat*$_2$, *R*,*B*,*C*,*K*,*G* is a potentiometer. The resistance wire, *AB*, is of uniform resistance per unit of length. Before making a measurement the drop in E.M.F. from *A* to *B* is set at some convenient value, e.g., 2 volts, by inserting a standard cell (not shown in Fig. 60) between *A* and *G* in place of the cell 2,3. With the standard cell between *A* and *G* and with *C* set so that distance *AC*: distance *AB* = E.M.F. of Standard Cell: E.M.F. desired for *AB*, *R* at the right is adjusted until upon tapping the key, *K*, the galvanometer shows no deflection. The cell 2,3 is then switched in between *A* and *G* and a point is found for contact *C* such that there is no deflection of *G* upon closing the key, *K*. Suppose that at this point *C* were half way between *A* and *B*, with the fall *A* to *B* set at 2 volts; obviously the cell 2,3 would have the E.M.F. of 1 volt. In general dist. *AC*/dist. *AB* × E.M.F. (*A* to *B*) will give the E.M.F. of the cell 2,3 at any time when *G* shows no deflection upon closing *K*.

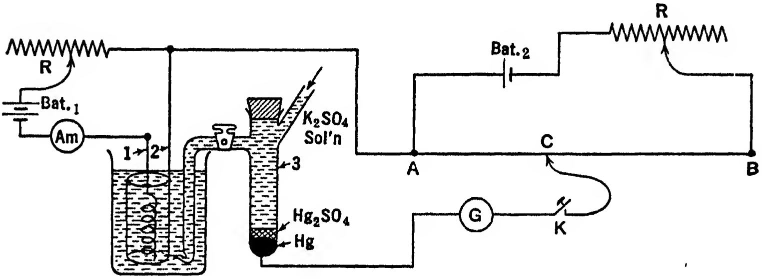

FIG. 60. Apparatus for Studying Cathode or Anode Processes. The circuit for the electrolysis is similar to that shown in Fig. 56. The auxiliary, or reference electrode, 3, functions in the same manner as the calomel electrode which is described in Fig. 45 (Chapter X).

The E.M.F. of cell 2,3 cannot be measured accurately by direct attachment of an ordinary voltmeter because the instrument draws so much current that it polarizes the cell. A voltmeter might be bridged between *A* and *K*, Fig. 60. Then upon balancing the E.M.F. of cell 2,3 by an opposed E.M.F., *AC* with the aid of the galvanometer and key, *K*, the current to operate the voltmeter is drawn from Bat_2 instead of the cell, 2,3. A vacuum-tube voltmeter could be used to measure the E.M.F. of cell 2,3 because a device of this sort draws practically no current from the cell that is measured. Since the potential of the reference electrode is known this gives the potential of the cathode. In this way the extent of separation may be calculated at any stage in the electrolysis. Also, if other metals are present the electrolysis may be stopped before there is any possibility of another metal being deposited. Of course similar measurements may be made for the anode. Such graded potential separations are of great theoretical interest but are not widely used because of the complicated apparatus and the care and attention that are required.

Another type of separation is of great practical importance, namely that made under such conditions that one metal is practically completely deposited, after which hydrogen is evolved at the cathode and the other metallic ions are not deposited. This is often called a *constant current separation,* although the current does not remain strictly constant. It might be expected that this type of process would be limited to the separation of metals below hydrogen in the electrolytic potential series (Au, Ag, Hg, Cu, Bi, etc.) from those above hydrogen (Fe, Zn, Co, Ni, Ca, Sr, Ba, Na, K, etc.). It has been shown however, that the potential at which hydrogen is liberated is not fixed, due to its overvoltage and may be made to show wide variations by varying the electrode surface and the *p*H. Hence such active metals as iron and nickel may be deposited completely from their solutions in weak acids, and zinc from a more strongly acid solution. The possibilities of determination and separation are, therefore, much more extensive than might at first thought seem probable.

Complex Electrolytes. The relative stabilities of complex ions like cyanides, metal-ammonia ions (as $Ni(NH_3)_4{}^{++}$), oxalates, fluorides, etc., are made use of in electrolytic separations. Complex cuprous cyanide ion is much less ionized into simple ions than the corresponding silver cyanide ion, and the voltage applied is roughly regulated between 1.1 and 1.6 to give a complete separation of the silver; the copper may be deposited by applying a much higher voltage, 3-4.5 volts.

Character of the Deposit. The physical characteristics of the deposit on the electrode are generally more satisfactory when the substance is deposited from a solution containing complex rather than simple ions. A better silver deposit is obtained from a silver cyanide solution than from a silver nitrate solution. Nickel, when deposited from solutions containing $Ni(NH_3)_4{}^{++}$, is in a very satisfactory form for drying and weighing.

Simultaneous deposition of an excess of hydrogen together with a metal may cause the latter to separate in a spongy form, readily oxidized or loosened from the electrode. It is well known that purer and more satisfactory copper deposits are obtained from a solution containing both sulfuric and nitric acids (or ammonium nitrate), than from one containing only sulfuric acid. The nitric acid or the nitrate reacts with the hydrogen as it is liberated: $H^+ + NO_3{}^- + 8e = NH_4{}^+ + 3H_2O$; bubble formation is prevented. It is interesting to note that because of this reaction a solution containing nitric acid and nitrates may become alkaline; this fact is significant when the solution contains metals which either give precipitates in ammoniacal solution or are deposited from such solution. For example, copper may be separated from iron and nickel in acid solution. In alkaline solution the iron would precipitate as hydrous oxide and the nickel would be deposited as metal on the cathode.

Heating to 80-100° C. in many cases improves the purity and physical properties of the deposit. The effect is in part due to mechanical stirring and in part to changed ionization, conductance, and overvoltage effects.

Other things being equal, mechanical stirring often improves the character of the deposit. The agency of heat, the rotation of either or both electrodes, or stirring by a motor-driven stirrer or a current of inert gas, or magnetic effects have been used successfully. The outstanding advantage of stirring the solution is that a very high current density ($N.D._{100}$ of 5 to 10 amps.) may be used without injuring the purity or physical character of the deposit. A great saving of time is possible, since the complete deposition of 0.1 to 1 g. of most metals may thus be effected in much less than an hour, whereas 4-8 hours are necessary for the same amount of metal at the low current densities that must be used when stirring is omitted. In the latter cases the use of a high current density causes spongy or tree-like deposits, presumably because of the local removal of metal ions from the solution near the electrode and the consequent deposition of hydrogen, since the ions of the latter are always present. With stirring, a liberal supply of metal ions is brought to the cathode, and the current is used principally in the deposition of metal.

Internal Electrolysis. The idea of allowing one metal to dissolve and to cause a more easily reducible metal to deposit on a platinum foil is often used in qualitative analysis. Such electrochemical displacement is also applied in quantitative work. In the latter, the metal that dissolves is connected by a wire to a platinum gauze or a dish upon which the more noble, or easily reducible metal or metals, may be obtained in a weighable form, with suitable technique. Although this method was first proposed in 1868 by Ullgren[1] its advantages and applications have not been appreciated until fairly recent years.[2] The determination of small quantities of the metals that are deposited either from solution, or which are in the metal which is dissolved are the chief uses of the method. Solutions which attack the platinum anode in an ordinary electrolysis may in many instances be used in the internal method. It is possible to control the cathode potential by the proper choice of a soluble metal, e.g., Pb, Zn, Cd, etc., provided these metals are free from impurities that deposit at the cathode. The method has been applied to such problems as: The separation of small amounts of Bi and Cu (and Ag, if present) from a large amount of lead; estimation of cadmium in zinc; copper in alloys high in zinc; tin in aluminum; separation of lead from antimony.

Review Questions and Problems

1. What weights of each of the following would be deposited by 241,250 coulombs: Cu^{++} ; Pb^{++} (at the anode as PbO_2); Au^{+++}; Sb^{+++}; Sn^{++++}?

2. How much time is theoretically required for a current of 0.01

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[1] C. Ullgren, Z. analyt. Chem. **7,** 442 (1868).

[2] For detailed applications, see Sand and collaborators, The Analyst, **55,** 309, 312, 495, 680 (1930); **56,** 90 (1931). Clarke, Wooten and Luke, Ind. Eng. Chem. Anal. Ed. **8,** 411 (1936). Clarke and Wooten, Electrochemical Society, **76,** 63 (1939). A review with bibliography.

ampere to deposit 0.2000 g. of copper from a solution of cupric sulfate? Ans. 16 hrs. and 52 min.

3. How many grams of each of the following would be deposited in 5 hours by an unvarying current of 0.05 ampere: Ag^+; Cd^{++}; Au^{+++}?

4. How much current does a 100 watt lamp use at 110 volts? What is the resistance of the lamp under these conditions? Ans. 0.909 amp.; 121 ohms.

5. Is it possible to deposit zinc from a slightly acidified solution upon either a copper or a platinum electrode? Reasons?

6. A current operating for a period of 15 hours deposited 2.400 g. of silver and liberated 0.500 g. of hydrogen. Calculate the average current in amperes. Ans. 0.925 amp.

7. A solution was originally 0.001 *M* in silver ion at 25° C. (*a*) What potential was needed at the cathode to deposit silver? (*b*) How much silver remains in 100 ml. of solution when the cathode potential has been brought to 0.5000 volt relative to the hydrogen electrode? Ans. (*a*) Initial $E_{Ag} = 0.6222$; (*b*) 0.0000925 g.

8. A 0.1 *M* solution of cupric sulfate is to be electrolyzed. Assuming complete ionization of the salt, molar concentration of H^+, an *IR* drop requiring 0.5 volt to overcome, and an oxygen overvoltage of 0.42 at the anode, what is the minimum applied voltage that will cause electrolysis?

9. An alloy contains copper, lead (less than 0.5 per cent), nickel and about 1 per cent of iron. Outline a scheme of analysis, making use of electrolytic methods as far as possible.

10. A given current deposited 0.2157 g. of silver. Assuming that the corresponding anode process was the liberation of oxygen, all of which escaped from the solution, (*a*) What weight of oxygen was liberated? (*b*) What volume would it occupy at standard conditions? Ans. (*a*) 0.0160 g. (*b*) 11.2 ml.

11. Upon electrolysis in ammoniacal solution arsenates are not reduced. Give a probable explanation and write a list of elements that might be separated from arsenic under these conditions.

12. At a current density of 0.01–0.1 amp. per sq. cm. the overvoltage of hydrogen on cadmium is more than 1 volt. Discuss the significance of this fact. Calculate whether cadmium could be deposited completely from a solution 0.01 *M* in H^+.

13. In what units is current density commonly expressed? Calculate the current densities at the anode and cathode the former having an area of 1.25 sq. cm. and the latter of 38.2 cm. with a current of 0.20 amperes flowing. Ans. 0.16 amps./sq. cm.; 0.0052 amps./sq. cm.

14. Repeat the calculations in problem 13 for electrodes of 0.50 and 25.0 sq. cm. respectively. If the connections were reversed what would be the effect of such conditions upon the deposition of a metal upon the smaller electrode?

15. How completely might it be possible to deposit copper before tin is deposited, the solution being 0.01 *M* in stannous ion?

16. If a current of 0.20 amp. deposits 0.500 g. of silver in one hour,

what is the current efficiency for depositing silver? Ans. 62.1 per cent.

17. How much copper is theoretically deposited by 0.10 amp. in 10 hours from a cupric solution? How much lead would be deposited as PbO_2 in 20 minutes by the same current? If the current liberated 1.050 g. of copper what was the current efficiency?

18. How much ferric sulfate could be reduced to ferrous sulfate by a current of 0.5 ampere acting for 5 hours?

19. Three electrolytic cells are connected in series. In one cell 1.065 g. of silver is deposited at the cathode, a like amount being dissolved at the silver anode; in the second cell copper is deposited, and in the third iodine is liberated at the anode. How much copper would be deposited? How many ml. of 0.1000 N sodium thiosulfate would be required to titrate the iodine that is liberated in the third cell?

20. Describe an experimental arrangement that might serve to determine the equivalent weight of cadmium.

21. Given a 2.2 volt storage battery, resistances and other instruments, sketch a circuit that might enable one to carry out an electrolysis at a total applied voltage not greater than 1.4. How could the effective cathode potential be measured and referred to the value for the hydrogen electrode?

22. If cadmium were used as the soluble anode, how completely (in per cent) might lead be deposited as the metal from a solution initially 0.00001 M in lead ion, the final cadmium ion concentration being 0.1 M? Ans. 99.99955 per cent of the lead deposited.

23. In preparing pure salts from fairly pure specimens of active metals it is desirable to add slightly less acid than is necessary to dissolve all of the active metal. Explain.

24. If in the apparatus indicated in Fig. 56, p. 412, the ammeter reads 0.25 amperes, B is 4.4 volts and the resistance of V is 1000 ohms, calculate the resistance between the electrodes, the part of R that is in series with the cell being 4.5 ohms. (Assume the resistances of the connecting wires, the ammeter and the electrodes in the beaker to be negligible). *Note.*—Resistances in series are additive in effect: In parallel the resistance R of a circuit is related to the parallel resistances r_1, r_2, etc., as follows:

$$\frac{1}{R} = \frac{1}{r_1} + \frac{1}{r_2} \text{ etc.}$$

Ans. 13.3 ohms.

25. For the same circuit as in problem 24, if R were 6.0 ohms, and V 1000 ohms, and that between electrodes in the solution 10 ohms, calculate the current in amperes if the battery B is 4.4 volts (neglecting the resistances of the ammeter connecting wires and electrodes). Approximately what voltage will be indicated on the voltmeter V?

CHAPTER XX

ANALYSIS OF ALLOYS
ELECTROLYTIC DETERMINATIONS AND SEPARATIONS

THE ELECTROLYTIC DETERMINATION OF COPPER

It is desirable to study the electrolytic process with the use of a pure substance, as for example crystallized or anhydrous copper sulfate.

Principle. The general principles of electroanalysis have been explained in Chapter XIX. If a solution of copper sulfate containing sulfuric and nitric acids is electrolyzed, the following reactions occur:

(a) cathode reactions: $Cu^{++} + 2e = \downarrow Cu.$
$2H^+ + 2e = H_2.$

secondary reaction:

$$10H^+ + NO_3^- + 8e = NH_4^+ + 3H_2O.$$

(b) anode reactions: $H_2O = 2H^+ + \frac{1}{2}O_2 + 2e$
$2NO_3^- + H_2O = \frac{1}{2}O_2 + 2H^+ + 2NO_3^- + 2e.$

The oxygen, as was stated in that chapter, is partially converted into ozone, but the major portion appears as molecular oxygen. It was also shown that the deposition process is virtually a complete one, p. 422.

Errors. The acid concentration of the solution must not be too great. Otherwise the deposition of copper will be incomplete, or the deposit will not adhere to the cathode. The current must not be interrupted while the electrodes are in contact with the acid solution; if this point is overlooked, the copper will dissolve to some extent. Care must be taken not to oxidize the surface of the copper while it is being dried prior to weighing.

The solution to be electrolyzed should contain only a trace of chloride ion, as the anode is apt to be corroded by the chlorine liberated during the electrolysis. A trace of chloride is, however, desirable.[1] For the same reason a mixture of nitric and hydrochloric acid attacks platinum. Anodes of platinum are attacked more readily than are those of a platinum-iridium alloy. Attack of anodes has been reported in the literature as occurring during electrolysis of ammoniacal solutions, cyanide solutions, solutions containing hydrofluoric acid, and perhaps others. In critical work it is necessary to examine solutions of electrolytic deposits for platinum, part of which appears as a black film if as much as a milligram is present. This source of error will not be encountered in the determinations described in this chapter as care is taken to avoid the presence of more than a trace of chloride ion.

Failure to remove nitrous acid from the nitric acid used may cause very peculiar phenomena during electrolysis. The copper may begin to deposit in good form and then dissolve in part, or the initial deposition may be delayed. Nitrous acid may be removed from nitric acid by boiling the latter. If this precaution has not been observed, the addition of urea to the solution will destroy the nitrous acid:

$$(1)\quad 2HNO_2 + (NH_2)_2CO = 3H_2O + 4N_2 + CO_2.$$

The error due to nitrous acid is increased by the presence of a large amount of iron, such as is found in solutions of certain copper ores. The iron is reduced by the electric current to the ferrous condition, whereupon nitric acid is reduced, and the copper deposit begins to dissolve. This error may be avoided by the proper regulation of the acidity and by the addition of ammonium nitrate instead of nitric acid, or by the removal of the iron prior to the electrolysis or by adding phosphate or fluoride to form a complex with the ferric ion[2] (see books on electroanalysis cited in the Appendix).

The elements which interfere in this method will be discussed in connection with the determination of copper in brass, p. 443.

Procedure. If crystallized copper sulfate is to be analyzed, weigh an approximately 0.5 g. sample into a 150-200 ml. beaker of tall form. Add 100 ml. of water, 1 ml. of concentrated sulfuric acid, 1 drop of 0.1 *N* hydrochloric acid and 5 drops of concentrated nitric acid which has been boiled to remove all nitrous

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[1] Scherrer, Bell and Mogerman, J. Research Natl. Bur. Standards, **22,** 697 (1939).

[2] H. A Frediani and C. H. Hale, Ind. Eng. Chem. Anal. Ed. **12,** 763 (1940).

acid. Warm and stir the mixture until solution is complete. If a platinum gauze cathode is to be used, clean the electrode by heating it in dilute nitric acid and washing it with distilled water. Dry the electrode at 100-110° C., cool, and weigh. Do not handle the gauze with the fingers, because a trace of grease may cause a non-adherent deposit of copper later.

Tantalum electrodes should not be cleaned with nitric acid. To remove a copper deposit the electrode is immersed in a mixture of equal parts of concentrated ammonia and water to which has been added 10 per cent of trichloracetic acid. This solution may be used repeatedly until its solvent power is lost. The electrodes are then washed with distilled water, dried and weighed.[1]

Arrange the circuit as shown in Fig. 56, p. 412. When the electrodes are in place, the beaker covered with a suitable split or slotted watch glass, and the circuit in order (for details, see the procedure for the electrolytic determination of copper in brass), electrolysis may be made either by the slow or the rapid method. (*a*) *Slow electrolysis, without stirring.* With an applied potential of 4 volts and all of the resistance in series when the circuit is closed, lower the resistance gradually until the ammeter shows a current of about 0.2 ampere. With such a current the operation if started late in the evening will be concluded early the following day. If conditions do not permit this practice, use a current of 1.5-3 amperes with a gauze electrode; deposition is usually complete in 1.5-3 hours. (*b*) *Rapid electrolysis; solution stirred.* If some device for stirring the solution is available, as, for example, a motor driven anode support, the anode being in the form of a paddle or cylinder, a much greater current may be used. After the solution is in position and covered, start the stirrer and adjust the speed to 400-800 r.p.m. Close the circuit with an applied potential of 10-12 volts, or even higher. Lower the resistance until a current of 5-10 amperes is obtained. The electrolysis is usually complete in 30-45 minutes. Before testing for complete deposition of copper as directed below, reduce the current to about 0.5 ampere and stop the stirrer.

Whether slow or rapid electrolysis is used, rinse off the cover glass into the solution after deposition is thought to be

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[1] L. W. Strock and H. S. Lukens, Electrochem. Soc. **56**, 409 (1929).

complete due to the color of the copper ion having disappeared. In this way the level of the liquid is raised so that about 0.5 cm. of bright cathode surface is immersed. Then continue the electrolysis for 30 minutes if a small current (0.2 ampere) is used, or for 10-15 minutes with a current of 1.5 amperes or more. If no copper appears on the fresh surface of the electrode, the deposition is usually regarded as complete. Chemical tests may be made on small portions of the solution if it is not to be used for further analyses.

If deposition is complete as proved by test, the liquid must be removed. Two methods are used. (1) The liquid may be siphoned off, care being taken that the current is never broken until all of the acid has been removed. Otherwise some copper will dissolve. A glass siphon provided with a stopcock is best, but a rubber tube may be used instead. While siphoning the heavier liquid from the bottom of the beaker, pour in water at the top to keep the level of liquid in the beaker nearly constant; continue this process until the ammeter needle drops practically to zero. Then rinse the cathode with a little acetone and dry it at 100-110° C. The drying should not be prolonged because of danger of oxidation of the metal; 5-10 minutes usually suffices. This method of washing the electrode is not as satisfactory when further determinations are to be made with the same solution, because the volume of liquid becomes so great that much time is lost in the subsequent evaporation. (2) First use an all-glass siphon to remove the electrolyte, and at the same time direct a continuous jet of water from a wash bottle around the upper edge of the electrode. Do not delay this washing until most of the solution has been removed from the electrode. If each portion of the exposed copper deposit is rinsed free from acid the instant the liquid is withdrawn from it, the acid will exert no solvent action on the copper. On the other hand, if this acid solution is not rinsed off immediately and before the circuit is broken, low results will be obtained. Then remove the beaker and replace it with one containing distilled water and finally rinse the electrode with a little acetone. Dry it at 100-110° C. for 5-10 minutes, cool and weigh. This latter method should be used when copper is being separated from other ions in the solution which are to be determined subsequently. Calculate the percentage of copper from the data obtained.

Clean the platinum gauze electrode by allowing it to remain for a few minutes in warm, dilute nitric acid. Then rinse it thoroughly with distilled water and dry it. For cleaning tantalum electrodes, see p. 432.

THE ANALYSIS OF BRASS

Brass is essentially an alloy of copper and zinc, but it usually contains small amounts of lead, tin, and iron. Antimony, nickel, and aluminum are sometimes present. An analysis includes, therefore, the separation and determination of tin, lead, copper, iron, and zinc. If any antimony is present, it will be weighed with the tin, and any aluminum will be precipitated with the iron.

Separation and Determination of Tin. When tin and its alloys are dissolved in nitric acid, insoluble stannic acid, H_2SnO_3, is formed:

$$(2)\quad 3Sn + 4HNO_3 + H_2O = \downarrow 3H_2SnO_3 + 4NO.$$

This precipitate, owing to its colloidal character, is not only difficult to filter but it shows a strong tendency to adsorb salts of certain metals, and usually contains more or less iron, lead, and copper, especially iron. If only nitric acid is present in the solution, precipitation is complete without an evaporation to dryness; such an evaporation would increase the amount of impurity in the precipitate and should therefore be avoided. In order that the stannic acid may be completely precipitated, the solution must be heated and be allowed to stand for some time. Ashless paper pulp is added to facilitate filtration, and the precipitate is washed with dilute nitric acid to prevent it from becoming colloidal. It is ignited at the highest temperature of the Meker burner to stannic oxide, SnO_2, and weighed as such. Care should be taken to avoid reduction of the oxide by the carbon of the filter paper and by flame gases:

$$(3)\quad H_2SnO_3 \text{ (ignition)} = SnO_2 + H_2O.$$

The precipitate should be pure white, but rarely is. The results obtained by this method are therefore invariably a little high; the other determinations are slightly low on this account. If a little antimony is present, the precipitate will consist of stannic oxide and antimony oxide, Sb_2O_4. If iron is present, some ferric oxide will be included and will be shown by the color. With careful work, very little cupric oxide and lead oxide will be in the precipitate.

The amount of the impurity may be determined by fusing the precipitate in a covered porcelain crucible at a red heat with ten times its weight of a mixture of equal parts of sodium carbonate and sulfur. Sodium polysulfide, Na_2S_4, is formed, which reacts with stannic oxide to give the soluble sodium thiostannate, Na_2SnS_3, and forms insoluble sulfides with the other metals. The above mixture is used instead of sodium sulfide because the latter is deliquescent. Since the yellow polysulfide dissolves some cupric sulfide, the solution is boiled with enough sodium sulfite to form the colorless sulfide,

$$(4)\quad Na_2S_2 + Na_2SO_3 = Na_2S + Na_2S_2O_3;$$

then the sulfides of iron, lead, and copper are filtered off, ignited to oxides and weighed, and their weight subtracted from that of the impure stannic oxide.[1] Any antimony present will be in the filtrate as sodium thioantimonate, Na_3SbS_4.

A more convenient method[2] is to add to the impure weighed tin oxide ten times its weight of pure ammonium iodide, and heat for 15 minutes in an electric oven at 425-475° C. Tin and antimony are volatilized quantitatively as stannic and antimonous iodides; the residue, after treatment with nitric acid, if necessary, is weighed as mixed oxides of copper, lead, and iron. The loss in weight is equivalent to the stannic and antimony oxides driven off.

The volumetric determination of tin is capable of greater accuracy than the gravimetric determination.

This gravimetric method separates tin more or less completely from most of the other elements except antimony, arsenic, and phosphorus. The antimony forms an insoluble acid similar to stannic acid, and the latter two elements form arsenic and phosphoric acids, which may be completely adsorbed by or coprecipitated with stannic acid if a sufficient amount of it is present.

Errors. Positive error: adsorption of other metals. Negative errors: 1. Incomplete precipitation of stannic acid caused

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[1] Craig, J. Ind. Eng. Chem. 11, 750 (1919).

[2] Caley and Burford, Ind. Eng. Chem., Anal. Ed. 8, 114 (1936).

by filtering the precipitate too soon or by the presence of other acids in addition to nitric acid; 2. Reduction during ignition.

Procedure. Tin Separated as Stannic Acid. The brass should be free from oil, but it need not be dried. Oil is removed by washing the alloy with ether or benzene. The samples given out are clean and ready for use.

Weigh out samples of about 1 g. each into 150 ml. beakers, and add 15 ml. of concentrated nitric acid, while keeping the beaker covered. The acid may be added all at once if the pieces of brass are not very small; otherwise it is best to add it 5 ml. at a time to avoid too violent a reaction. Keep the solution somewhat below the boiling point until it has evaporated to about 5 ml.; do not allow it to evaporate to dryness. If this should occur, repeat the experiment with a new sample. The evaporation should require at least one hour to make certain that all stannic acid has precipitated; longer standing does no harm. Dilute the solution to about 35 ml., and keep it hot for 20 or 30 minutes, in order that all soluble salts may dissolve. Then add filter paper pulp prepared from a piece of a filter paper tablet. These tablets are made for this purpose and are ashless. Tear off a small piece, put it in a test tube with a suitable amount of distilled water, and shake the mixture vigorously for a minute. A much better pulp is obtained in this way than by disintegrating a filter.

Add a suitable amount of the pulp to each of the solutions containing the precipitate of stannic acid, and stir the mixture. It is possible with such treatment to obtain a clear filtrate without clogging the filter, a result that could not be achieved otherwise. Paper pulp is useful with precipitates of a colloidal or gelatinous nature, but need not be used with those that filter readily. Sometimes, however, it is advisable to pour a little pulp on the filter paper before beginning a filtration.

Stir up the precipitate and filter it through a small, close-textured filter paper or a double filter into a 150 ml. beaker; pass the first portion of the filtrate, if not clear, through the paper a second time. If the amount of tin is large, more pulp may be required. Wash the precipitate thoroughly at least 12 or 15 times with hot 1 per cent nitric acid, fold up the filter, and char it at a low heat in a porcelain crucible weighed without the cover. Burn off the carbon at a very low red heat to avoid reduction, and finally ignite the residue for half an hour at the full heat of the Meker burner, while keeping the crucible in a slanting position so as to permit the free access of air (Equation (3)). Do not cover the crucible or heat it in a covered clay cylinder, for the stannic oxide is very easily reduced by the flame gases. If reduction occurs, the precipitate may be moistened with a drop of nitric acid and ignited again. Ignite to constant weight and weigh as stannic oxide. Calculate the percentage of tin. The conversion factor is 0.7877. If iron is present in the brass, a little of it is usually carried down with the stannic acid, and the ferric oxide gives a brownish or a pink color to the stannic oxide. This impurity cannot be removed by treatment with acid. If the oxide is dark gray, which is rarely the case, it is contaminated with black cupric oxide and careless manipulation is thus indicated.

When an exact determination of the total amount of impurity in the stannic oxide is required, how should it be carried out?

Separation and Determination of Lead. Separation as Lead Sulfate. The solution after the removal of the tin, or, if no tin is present, the nitric acid solution of the brass, is evaporated with an excess of sulfuric acid to convert all of the metals into the sulfates. It is necessary to expel all other acids, since they increase the solubility of lead sulfate. The reaction of the sulfuric acid with the lead nitrate is

$$(5)\quad Pb(NO_3)_2 + H_2SO_4 = \downarrow PbSO_4 + 2HNO_3,$$

and similar equations hold for the other metallic nitrates.

The soluble sulfates are dissolved in water, insoluble lead sulfate remaining. Two or three ml. excess of concentrated sulfuric acid should be present in every 100 ml. of solution to reduce the solubility of the precipitate and to prevent contamination of it by other metals. The precipitate is finely crystalline and very dense. It is washed with cold dilute sulfuric acid—1 ml. of concentrated acid to 200 ml. of water—to reduce its solubility. One hundred ml. of such a wash solution dissolves at 18-20° C. about 0.5 mg. of lead sulfate, at 12° C., 0.35 mg., while the same volume of water at 20° C. dissolves 4.5 mg. of lead sulfate. When the concentration of sulfuric acid is over 20 per cent, the solubility of the precipitate begins to increase, and in the concentrated acid it is quite appreciable.

If the precipitate is filtered through paper, all the acid must be washed out of the filter, or it will be extremely difficult later to burn off the carbon. Alcohol or acetone must be used for this purpose, as water would dissolve too much of the precipitate. Some reduction by the carbon of the filter paper is unavoidable, and any lead must be converted back to the sulfate by treatment with nitric and sulfuric acids. A filtering crucible which eliminates this difficulty should, therefore, be used.

The final ignition of the precipitate should be at a barely visible red heat—500-600° C.—and all reducing gases must be carefully excluded. Lead sulfate may be heated at 700° C. in an oxidizing atmosphere without appreciable decomposition, but at a higher temperature it begins to lose sulfur trioxide, and a basic sulfate remains.

Lead sulfate may be separated from tin by having sufficient sulfuric acid in the solution to prevent the stannic sulfate from hydrolyzing to form stannic acid. At least 15 per cent of acid is required or about 9 ml. of concentrated acid per 100 ml. of solution, and the solution must be kept cool after dilution. A concentration of 8 per cent of acid will suffice to separate lead sulfate from bismuth and antimony. The lead sulfate may be freed from traces of tin, bismuth, or antimony by dissolving it in ammonium acetate and filtering off the stannic hydroxide and other impurities, after which the lead is reprecipitated with sulfuric acid. Such treatment serves also as a fairly satisfactory separation of lead sulfate from barium sulfate and from other insoluble substances.

The gravimetric determination of lead as lead sulfate is the most accurate of all the methods for that metal. This is especially the case when the precipitate is weighed in a filtering crucible. Lead is separated as the sulfate from all common metals except barium, strontium, and appreciable amounts of calcium.

Errors. The only positive errors are those due to contamination of the precipitate with some other metal, or possibly to incomplete expulsion of the sulfuric acid. The negative errors are: 1. Solubility of the lead sulfate; 2. Reduction of the lead sulfate during ignition of the precipitate; 3. Dissociation of the lead sulfate due to ignition at too high a temperature.

Procedure. Lead Separated as Sulfate. Add to the filtrate from the stannic acid, or, if tin was absent, to the nitric acid solution of the brass, 2-3 ml. of concentrated sulfuric acid, and evaporate the solution on the low temperature hot plate until the cover glass is dry, in order to expel all nitric acid. (Why?) The color of the residue should be gray or white, not blue. (Equation (5)). Do not evaporate the material to dryness. The salts should be slightly moist with concentrated sulfuric acid. If this is not the case, cool the solid, add 10 or 15 ml. of water and 1 ml. of concentrated sulfuric acid, and evaporate the solution again. Do not evaporate too rapidly toward the end of the process or spattering will occur. Cool, add very carefully 20 ml. of water, heat the mixture for 10 or 15 minutes, and then dilute the solution to 80-100 ml. Apply heat until everything except the lead sulfate has dissolved. This precipitate is crystalline and very dense. Let the solution stand until cold, for at least one hour, and then filter it through a Gooch or other filtering crucible into a 400 ml. beaker. Wash the precipitate 10 or 12 times with cold, dilute sulfuric acid—1 ml. of the concentrated acid to 100 ml. of water—until all copper and zinc salts are removed, and reserve this filtrate for the determination of these metals. Place the filtering crucible inside an ordinary crucible to protect it from flame gases, and heat it to 500-600° C., or until the bottom is a barely visible red, for 20 to 30 minutes, or heat it in the electric muffle at 500° C. Cool the residue and weigh as lead sulfate. Repeat the ignition until the weight is constant. Calculate the percentage of lead. The conversion factor is 0.6833.

The precipitate should be white, but it is often slightly colored by traces of iron or other metals. If it was heated at too high a temperature, some lead oxide would be formed. In such a case, treat the precipitate with a drop of concentrated sulfuric acid and heat again.

If a paper filter was used (it is not recommended), wash out the sulfuric acid by several applications of methyl or denatured alcohol or acetone. (Why?) It is well to rinse out the beaker with alcohol or acetone, and, if any precipitate remains, to wipe it out of the beaker with a small piece of damp filter paper, which is added to the filter. Fold up the paper, char it, and burn off the carbon at the lowest possible temperature, for lead sulfate is very easily reduced. Some reduction is unavoidable, and the metallic lead must be converted into lead sulfate. Add one drop of concentrated nitric acid and one drop of water to the precipitate, and warm gently to convert the lead into lead nitrate:

$$(6)\ 3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O.$$

After a minute or two add one drop of concentrated sulfuric acid, and evaporate the acid carefully; then heat the precipitate, uncovered, for half an hour, and increase the temperature gradually until the bottom of the crucible is a barely visible red (500-600° C.). Ignite the material to constant weight, and weigh as lead sulfate. If heated at too high a temperature, treat the precipitate with a drop of concentrated sulfuric acid and heat again.

✓ **Separation of Lead Electrolytically.** (See Chapter XIX.) The determination of lead by electro-deposition of lead dioxide at the anode is a rapid and accurate method. If 15 ml. of concentrated nitric acid is used in each 100 ml. of the electrolyte, the lead is deposited entirely on the anode, and a certain amount of copper is deposited on the cathode. The presence of 8 or 9 drops of concentrated sulfuric acid in the solution makes the deposit of lead dioxide more adherent. A current of 1.5 to 2.0 amperes for one hour is usually sufficient in the analysis of a sample of brass. The platinum gauze and the deposit are dried at 120° C., and a conversion factor of 0.8640 instead of the theoretical factor of 0.8660 is used in calculating the weight of lead from that of the lead dioxide, since the deposit usually contains a slight excess of oxygen or a trace of water. When only a few milligrams of lead are present or if it is desired to deposit the copper simultaneously, the concentration of nitric acid in the solution should not exceed 3 per cent. Such small amounts of lead, however, are usually not completely deposited. If the acidity of the solution is too low, a part of the lead may be deposited as metal on the cathode, and in the absence of any oxidizing agent half of it may be so deposited.

The electrolytic method for lead is available in the presence of all of the common metals except silver, bismuth, and manganese, which form peroxides at the anode; and chromium, antimony, arsenic, tin and phosphate or chloride ion, which either contaminate the deposit or hinder precipitation. In the present case, therefore, lead is separated in the filtrate from the stannic acid.

Procedure. Lead Separated Electrolytically. Evaporate the filtrate from the determination of tin to 50 ml. Transfer the solution to a 150 ml. beaker of the tall, narrow type. Add 8 or 9 ml. of concentrated nitric acid for each 75 ml. of solution, and then 5 or 6 drops of concentrated sulfuric acid. The total volume of the solution should not exceed 100 ml. In the meantime secure a platinum gauze electrode and a heavy platinum wire. Clean them by boiling for a few minutes in dilute nitric acid and rinse them thoroughly. Dry the gauze electrode in the oven for 20 or 30 minutes, cool and weigh it. Let the electrode stand a few minutes in the balance case before weighing it. Do not bend the wire handle and do not try to put the electrode into a small desiccator. Do not leave it in the oven longer than necessary, for it is likely to be stolen. Do not secure the electrode until ready to use it, and return it as soon as the electrolysis is finished. With the source of current disconnected, insert the wire handle of the gauze electrode through one binding post on the holder which is clamped to a ring stand, and through the other binding post insert the straight platinum wire. The later should then form the axis of the cylinder, but should not extend below it. Lower the electrodes into the beaker until they just touch the bottom. The cylinder may be entirely covered but should be at least two-thirds immersed. With all resistance in the circuit, connect the positive terminal of the battery to the gauze anode and the negative terminal to the wire cathode. If the polarity of the terminals is not known, it may be determined by touching the two wires to paper moistened with potassium iodide solution. A brown stain of iodine will form at the positive pole. Adjust the resistance so as to obtain a current of 1.5 to 2.0 amperes. Continue the electrolysis for an hour or more. As the solution becomes warm, its resistance decreases and the current increases, so that further adjustment of the resistance is required at intervals. Rinse the cover glass into the solution once or twice during the process. Some copper will usually deposit on the wire cathode, but this will dissolve off if the wire is returned later to the solution after the anode has been removed. If a trace of manganese is present, it will be oxidized to permanganic acid, which colors the solution but causes no interference. When the electrolysis has been completed, slowly raise the electrodes without interrupting the current. At the same time rinse off the electrodes very thoroughly with a jet of water from the wash bottle; take care that all wash liquid falls without spattering into the electrolytic beaker, as the solution in this beaker and the washings contain the copper and the zinc which are to be determined later. As soon as the electrodes are out of the liquid, rinse the gauze electrode in a beaker of water and finally rinse it with a little acetone. Return the straight wire electrode, on which there may be a slight deposit of copper, to the electrolytic beaker. After the acid solution has dissolved the copper, remove the wire and rinse it thoroughly. Dry the gauze electrode in the oven for 20-30 minutes, cool and weigh it. By multiplying the gain in weight of the electrode, which is due to lead dioxide, by the factor 0.8640 (instead of the theoretical factor, 0.8660), the weight of lead in the sample is obtained. If the deposit is not adherent, electrolyze each of the remaining samples in a hot solution. In that case place the electrolytic beaker on a wire gauze with a small flame underneath. Keep the solution hot, but do not boil it. After the deposit has been weighed, it may be removed from the electrode by means of the nitric acid solution originally used for cleaning, provided a little hydrogen peroxide or sodium nitrite is added to reduce the lead to the bivalent form. The solution remaining after the deposition of lead dioxide is reserved for the determination of copper and of zinc.

Sometimes, especially when much lead is present, the deposit will fall off the gauze electrode in spite of the above precautions. If this occurs, remove the electrodes from the holder and dissolve the lead dioxide by adding a little hydrogen peroxide to the solution and heating. Remove the clean electrodes and determine the lead as lead sulfate as directed for that process. If only very small amounts of lead are present, deposition in the form of the dioxide is likely to be incomplete. With large amounts of lead a more adherent deposit will be obtained by carrying out most of the electrolysis with a current of 0.3-0.5 ampere, and increasing the current, when most of the lead has been deposited, to 1.5-2.0 amperes. A sand-blasted surface causes greater adherence than smooth platinum.

Separation and Determination of Copper. Electrolytic Separation. (See Chapter XIX.) The most accurate method for the determination of copper is that of electrolytic deposition. Such a procedure affords a separation of copper from lead, cadmium, zinc, and all metals except those having an electrode potential near that of copper or more positive than this. Considerable amounts of iron in solution, due to the oxidizing action of ferric ion or to the effect of nitrous acid formed by the interaction of ferrous ion and nitric acid, prevent the deposition of the last traces of copper. The interfering metals, silver, mercury, bismuth, antimony, arsenic and tin are more or less deposited at the potential required for copper. If these metals are present, they must be removed or the copper may first be separated by some other method, e.g., as thiocyanate. In the analysis of brass, the copper is usually deposited electrolytically after the tin and lead have been removed.

The deposition of copper is most satisfactorily made from a solution containing 2 ml. of concentrated sulfuric acid, 1 drop of 0.1 *N* hydrochloric acid[1] and 1 ml. of concentrated nitric acid per 100 ml. of solution. The nitrate ion acts as a depolarizer to prevent the evolution of hydrogen. The latter reduces the nitrate ion to an ammonium salt. If hydrogen is liberated at the cathode, the deposit of copper is likely to be dark and spongy. With a platinum gauze cathode of the usual dimensions, a current as great as 3 amperes may be used for the electrolysis. When the blue color of the cupric ion has disappeared from the solution, or when bubbles of hydrogen appear at the cathode, a rough test may be made for complete deposition by adding a small amount of water to the solution and noting after 15 minutes if copper is still being deposited on a clean portion of the electrode. At the end of the electrolysis it is important not to interrupt the current until the electrodes have been washed free from electrolyte. Otherwise the copper will dissolve to some extent. The gauze electrode is dried at 100-110° C. before weighing. Traces of copper not deposited by the electric current are recovered by treatment of the solution with hydrogen sulfide; the cupric sulfide obtained is ignited in a porcelain crucible to cupric oxide.

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[1] Scherrer, Bell and Mogerman, J. Research Natl. Bur. Standards, **22**, 697 (1939).

By using a hot, concentrated solution and stirring it mechanically, the current density may be greatly increased and the time required for quantitative deposition of the metal may be reduced to 15 or 20 minutes; ordinarily half an hour or more is required. The presence of ammonium nitrate or of ammonium sulfate is often desirable and the absence of chloride ion (except a trace), nitrite ion, and much ferric ion is essential. Silver, mercury, arsenic, antimony, tin, and bismuth interfere.

The separation of copper as cupric sulfide is not satisfactorily effected by hydrogen sulfide, but the separation as cuprous sulfide by sodium thiosulfate is better. The thiocyanate separation is better than any other except the electrolytic.

Procedure. Copper Separated Electrolytically. *If the lead has been determined electrolytically* add 3 ml. of concentrated sulfuric acid to the solution, and evaporate until all nitric acid is removed and the cover glass is dry. Cool the residue and treat it with water, and as soon as the salts have dissolved transfer the solution to a 150 ml. beaker of the tall narrow type. If any lead sulfate appears, it should be determined as directed for the sulfate method. Add 1 ml. or less of concentrated nitric acid. *If lead has been separated as the sulfate,* concentrate the solution to 75 ml. in a 150 ml. tall beaker and add 1 ml. of concentrated nitric acid. The object of the nitrate ion is to act as a depolarizer and thus prevent the evolution of hydrogen, which would cause a spongy deposit. Add 1 drop of 0.1 *N* hydrochloric acid, *no more.* The total volume of the solution should not exceed 100 ml. Clean, dry, and weigh the platinum gauze electrode as directed under the electrolytic determination of lead. With the source of current disconnected, attach the platinum electrodes to the holder in the same manner. In this case, however, connect the positive terminal of the battery to the platinum wire which is to serve as the anode, and the negative terminal of the battery to the platinum gauze which is to serve as the cathode. Lower the electrodes into the beaker, and be sure that they touch the bottom or nearly so. The gauze cylinder should be two-thirds to three-fourths immersed. Cover the beaker with a clean split or slotted watch glass. Put in all the resistance and close the circuit. Adjust the resistance so as to obtain a current of 1.5-2.0 amperes, or, if the electrolysis is run overnight, use 0.2-0.3 ampere. If a deposit of copper does not appear promptly, too much nitric acid is present in the solution. Continue the electrolysis for some time after the blue color of the copper ion has disappeared, or until bubbles of hydrogen appear at the gauze cathode. Gaseous hydrogen may not appear at all if much nitrate ion is present. The electrolysis usually requires an hour and a half or more. When it appears to be completed, rinse off the watch glass into the beaker. If no further deposit appears on the clean platinum surface exposed to the liquid after 20-30 minutes, the deposition may be considered finished. Be very careful about washing the copper deposit. If the current is interrupted while the cathode is in contact with the electrolyte, some copper will surely dissolve. Without interrupting the current, either lower the beaker or slowly lift the electrodes out of the liquid, or siphon out most of the solution with an all-glass siphon, while at the same time washing the electrodes very thoroughly with a jet of water from a wash bottle. As each new level of copper is exposed from the liquid, it should be washed thoroughly with distilled water to remove all nitric acid before a further surface of the deposit is exposed. It is best to direct a continuous jet of water from the wash bottle around the upper part of the electrode. As soon as the electrodes are out of the liquid, finish the washing by quickly bringing up the smallest suitable beaker filled with distilled water, and finally rinse the electrode with a little acetone or alcohol. Dry it for a few minutes in the oven at 110° C., cool and weigh it. The gain in weight represents the weight of copper in the sample, provided none is recovered from the solution. The deposit should be bright red and adherent. If it is dark red or spongy, dissolve it in nitric acid, and boil off all nitrous acid since it prevents the deposition of copper. Adjust the acidity again and repeat the electrolysis. Dark or spongy deposits result from (a) too high a current, (b) the presence of interfering metals mentioned above, (c) insufficient nitrate ion, and (d) sometimes too long duration of the current, the nitric acid by reduction to ammonia decreasing the acidity of the solution to such an extent that other metals may be deposited. Chloride ion, except a trace, must be absent. The chlorine liberated at the anode attacks the platinum and dissolves some of it, with the result that platinum is deposited at the cathode.

Any copper not deposited may be recovered by passing hydrogen sulfide into the solution for a few minutes, but this should not be done unless a test on 2 ml. of the solution indicates that it is necessary. If only white sulfur is formed no copper is present. The test solution should be returned to the main solution after the hydrogen sulfide has been removed from it by boiling. If a dark precipitate is formed, however, the entire solution should be precipitated, filtered through a small filter, and the precipitate should be washed with 1 per cent ammonium nitrate, and ignited to oxide in a porcelain crucible. The weight of copper thus obtained from the cupric oxide is added to the weight obtained on the electrode. The filtrate is evaporated to remove hydrogen sulfide and is then used for the determination of zinc. If the wire anode is covered with a brown film this is probably a little lead dioxide. If it is desired to determine this lead, it can be done by weighing the wire with the deposit and again after the dioxide has been dissolved off.

Separation of Copper as Thiocyanate. The essential conditions for the complete precipitation of copper as cuprous thiocyanate, CuCNS, are: 1. Slight acidity of the solution, since the solubility of the precipitate increases with the concentration of hydrogen ion; 2. The presence of a reducing agent to reduce the cupric to a cuprous salt, sulfurous acid being commonly used in the form of one of its salts, such as ammonium bisulfite; 3. The absence of every trace of nitric acid or of other oxidizing agent, the solution containing only sulfuric or hydrochloric acid; 4. A slight excess of ammonium thiocyanate, since a large excess increases the solubility of the precipitate, due to the formation of a complex thiocyanate ion. After the separation of the lead as lead sulfate, the solution contains only sulfates, and is ready for the precipitation of the cuprous thiocyanate as soon as the greater part of the acid present has been neutralized with ammonia. If no lead is present or if the lead was separated electrolytically, the solution of the nitrates must be evaporated with sulfuric acid to expel every trace of nitric acid. A solution of ammonium bisulfite (or sulfurous acid, if preferred), followed by ammonium thiocyanate, is added to the slightly acid solution. A white precipitate of cuprous thiocyanate is formed; the cupric ion is reduced to cuprous ion and the sulfite ion oxidized to a sulfate:

$$(7)\ 2CuSO_4 + 2NH_4CNS + NH_4HSO_3 + H_2O = \downarrow 2CuCNS + 3NH_4HSO_4.$$

The precipitate is curdy like silver chloride, and is readily coagulated by boiling. It is washed with a very dilute ammonium thiocyanate solution to reduce its solubility; a little ammonium bisulfite is added to the wash solution to prevent any oxidation of the cuprous salt. The precipitate is then ignited at a bright red heat with free access of air to cupric oxide and is weighed as such:

$$(8)\ 2CuCNS + 5O_2 \text{ (ignition)} = 2CuO + 2SO_2 + 2CO_2 + N_2.$$

If the crucible is covered during the ignition or if any reducing gases are present, reduction to metallic copper will occur. The cupric oxide will contain a little copper sulfate if the temperature of ignition is not high enough.

This method serves as a separation of copper from nearly all other metals except silver and mercurous mercury, the experimental conditions being varied according to the properties of the metals present. The precipitate of cuprous thiocyanate may be titrated with a standard permanganate or iodate solution. (Reactions?) If preferred, the reaction between silver nitrate and a thiocyanate may be utilized, p. 185.[1] Of the volumetric methods for copper, the iodometric method is the most widely used.

Errors. Positive error: Too low a temperature during ignition so that some undecomposed copper sulfate remains. Negative errors: 1. Incomplete precipitation due to too acidic a solution; 2. Incomplete precipitation due to insufficient sulfite as a reducing agent, or to the presence of nitric acid or other oxidizing agent; 3. Reduction of the precipitate during ignition.

Procedure. Copper Separated as Cuprous Thiocyanate. The filtrate from the separation of lead as lead sulfate will contain only the sulfates of copper, iron, and zinc, and is therefore ready for the precipitation of the copper as cuprous thiocyanate. If tin and lead are absent, of if the electrolytic method for lead has been used, evaporate the nitric acid solution with 3 or 4 ml. of concentrated sulfuric acid to fumes of the latter in order to expel

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[1] Edgar, J. Am. Chem. Soc. **38**, 884 (1916).

all nitric acid. This step is very important. It does not take long, but it must not be carried out so rapidly as to cause spattering of the mixture. Add a little water to the cold residue to dissolve the salts, and neutralize the cold solution with ammonia until a faint precipitate just persists, or, if no precipitate forms, until the light blue color of the cupric ion begins to turn to the darker blue of the cupric ammonia ion. Add not more than 1 ml. of concentrated sulfuric acid, which should be sufficient to dissolve any precipitate and to give a light blue solution. Then add 20 ml. of a solution of ammonium bisulfite, prepared for this purpose by diluting to ten times its volume the concentrated solution, which has a specific gravity of 1.32 and contains about 47 per cent of sulfur dioxide. Dilute the solution thus obtained to 200 ml., heat nearly to boiling, and add slowly, for each 1 g. of brass, 12 ml. of a 10 per cent solution of ammonium thiocyanate —equivalent to 1.2 g. of the salt (Equation (7)). Boil the liquid for a minute or two and stir it to prevent bumping. The precipitate of cuprous thiocyanate should be white; any brown color is usually due to the presence of a small amount of cuprous sulfide formed from the action of cuprous ion with a little thiosulfate which may be in the bisulfite. This substance, however, does no harm. Let the solution which should be colorless and should have an odor of sulfur dioxide, stand until cold—for at least 1 hour, or longer if preferred. Filter the precipitate and wash it 10 or 15 times with a cold solution prepared by adding to every 100 ml. of water 1 ml. of a 10 per cent ammonium thiocyanate solution and 5 or 6 drops of the ammonium bisulfite solution. (Why?) The precipitate is readily filtered and washed. Any precipitate adhering to the beaker may be wiped off with a small piece of filter paper which is then added to the main precipitate.

Fold up the paper in the funnel, transfer it to a weighed porcelain crucible, and burn off the carbon at a low heat. Then ignite the precipitate at the full temperature of the Meker burner for 1 hour, while keeping the crucible near the top of the burner and in a slanting position so as to obtain the maximum temperature with free access of air (Equation (8)). Revolve the crucible occasionally so as to heat all parts of the precipitate, and do not allow much of the flame to cover the mouth of the crucible. Only a Meker or similar type of burner will give the temperature required. Do not cover the crucible or heat it in a covered clay cylinder. Such a procedure will inevitably cause reduction of the cupric oxide to metal. Ignite the residue to constant weight to make sure that all of the sulfate is decomposed, and weigh the cupric oxide. Calculate the percentage of copper. The conversion factor is 0.7989.

The precipitate should be black; any trace of red in it is an indication of the reduction of some cupric oxide to cuprous oxide or copper. Both of these substances may be converted into cupric oxide by strong ignition in an oxidizing atmosphere.

The cuprous thiocyanate may be dissolved in nitric acid, and the copper deposited electrolytically after the solution has been evaporated to a small volume to destroy thiocyanate ion and sulfur. This procedure is to be preferred to the ignition of the thiocyanate to cupric oxide.

Separation and Determination of Iron. The iron is present in the ferrous form in the filtrate from the copper determination. If the thiocyanate method for copper was used, the excess of sulfite and thiocyanate ion is destroyed by an evaporation with nitric and hydrochloric acids, which also removes ammonium salts. The residue is dissolved in hydrochloric acid, and the iron is precipitated by an excess of ammonium hydroxide. The precipitate, which contains a good deal of zinc, is dissolved in hydrochloric acid and reprecipitated. Even this treatment does not usually remove all of the zinc, for, as already stated, iron and aluminum cannot be accurately separated from copper, cadmium, and the metals of the zinc group by the use of ammonia. Since the precipitate of hydrous ferric oxide is very small, the amount of zinc carried down with the second precipitate may be neglected without introducing a serious error. After ignition the precipitate is weighed as ferric oxide. If the copper has been separated electrolytically, any ferrous iron present will be oxidized by boiling the solution with a few drops of nitric acid. The remainder of the process will be exactly the same as given above.

Procedure. Iron Separated as Hydrous Ferric Oxide. The basic acetate method which gives a sharp separation from zinc should be used in cases where the amount of iron is appreciable. With the ammonia method the technique is simpler, but the precipitate will contain a little zinc, the amount depending on the size of the precipitate. Since there is usually very little iron in a brass, the error introduced by the zinc which is carried down by the hydrous ferric oxide may be disregarded if a double precipitation is made. If the amount of iron seems to be unusually large, a third precipitation is advisable. It has already been mentioned that zinc may be separated quantitatively from iron, aluminum, chromium, nickel, and manganese by precipitation as zinc sulfide from a slightly acid solution buffered with formic acid and ammonium formate.

All of the iron must be in the ferric form, whatever the method chosen to precipitate it. The preceding operations have reduced it more or less to the ferrous form and it must be oxidized. If the copper has been separated electrolytically, the solution will contain nitric acid, and the addition of a few drops more, followed by an evaporation to 50 ml. will usually be sufficient to oxidize the iron. As an additional precaution after this evaporation, it is well to add a little bromine water.

If the thiocyanate separation has been used, add 35 ml. of concentrated nitric acid and 15 ml. of concentrated hydrochloric acid to the filtrate from the cuprous thiocyanate, and evaporate the solution nearly to dryness. Thiocyanate ion, sulfite ion, and ammonium salts are removed by this evaporation, and a residue consisting of zinc sulfate, sulfuric acid, and a little ferric sulfate is left. To the cold residue add 2 or 3 ml. of concentrated hydrochloric acid, warm the mixture gently, and after a few minutes dilute the solution to 50 ml. Filter into a small beaker to remove silica and wash the precipitate thoroughly with 1 per cent hydrochloric acid.

The solution is now ready for the precipitation of hydrous ferric oxide. Add a sufficient excess of clear, concentrated ammonium hydroxide to precipitate the hydrous ferric oxide and to dissolve any zinc hydroxide which may precipitate. Boil the solution a moment, let the precipitate settle, and filter it through a small filter into a 400 ml. beaker. Wash the precipitate a few times with hot, 1 per cent ammonium nitrate, and then dissolve it by pouring over it a boiling hot mixture of 5 ml. of concentrated hydrochloric acid and 15 ml. of water. Allow the liquid to run into the beaker in which the precipitation was made. Wash the filter, first with 1 per cent hydrochloric acid and then with water. Precipitate the iron in the filtrate as before; keep the volume of the solution small. Filter the precipitate through the same filter into the first filtrate, and wash it thoroughly with hot 1 per cent ammonium nitrate and a drop or two of ammonia. Ignite the precipitate and weigh it as ferric oxide. Calculate the percentage of iron. The conversion factor is 0.6994.

Any aluminum present will be weighed as aluminum oxide with the ferric oxide.

Determination of Zinc. After removing the iron (and aluminum), only the zinc remains in the solution. If it is known that there is no iron in the brass, the filtrate from the copper determination is used directly, after concentrating it somewhat. The solution is neutralized with methyl red or methyl orange as indicator, and the zinc is precipitated as zinc ammonium phosphate by the addition of diammonium hydrogen phosphate. The acid formed during the precipitation reacts with excess of the precipitating agent to form ammonium dihydrogen phosphate. These two phosphates which are present act as a buffer to keep the solution neutral. The solution should have a *p*H of 6.4 to 7.0.

$$(9)\quad ZnSO_4 + 2(NH_4)_2HPO_4 = \downarrow ZnNH_4PO_4 + NH_4H_2PO_4 + (NH_4)_2SO_4.$$

Since zinc ammonium phosphate is soluble both in acids and ammonia, the solution must be carefully neutralized. The presence of a little acetate seems to be desirable. The flocculent zinc phosphate first formed soon changes to the crystalline double salt, $ZnNH_4PO_4 \cdot H_2O$. In the early part of the precipitation the solution becomes acid, and as more phosphate is added the indicator changes to yellow and remains so. (Why?) Methyl red should never be pink after the precipitation is complete. If the diammonium hydrogen phosphate is not known to have the proper formula, it should be tested with phenolphthalein, with which it should give a barely visible pink tint. This test distinguishes the salt from the more acid phosphate, $NH_4H_2PO_4$, which would not be suitable here. The zinc ammonium phosphate is washed with cold water in which it is very slightly soluble—far less so than the corresponding magnesium compound. One hundred ml. of water at about 15° C. dissolves an amount of zinc ammonium phosphate equivalent to 0.5 mg. of zinc. A correction for the solubility of the precipitate may therefore be applied by measuring the amount of wash water used. Alcohol is sometimes recommended as wash solution, but it is likely to be slightly acid.

The precipitate is then carefully ignited at a bright red heat to zinc pyrophosphate and is weighed as such. Care should be taken to avoid a reducing atmosphere during the ignition.

$$(10)\ 2ZnNH_4PO_4\ \text{(ignition)} = Zn_2P_2O_7 + 2NH_3 + H_2O.$$

Instead of igniting the precipitate it may be dried at 100-105° C. and weighed as anhydrous zinc ammonium phosphate.

This method of precipitating the double ammonium phosphate in a neutral solution applies also to cadmium and, less satisfactorily, to cobalt. In the cases of manganese and magnesium, an ammoniacal solution is used. All metals but the one being determined must be absent. In other words, this is not a separation except from nickel because all metals except the alkalis are precipitated by the reagent, although nickel is not precipitated under the conditions used here.

Zinc may be precipitated as zinc sulfide in a dense, granular form from a solution in which the *p*H is 2-3.[1] If the *p*H is much less than 2, precipitation of the zinc is incomplete; if more than 3, the precipitate becomes gelatinous and is difficult to filter. All metals of the acid hydrogen sulfide group are precipitated with the zinc. This method affords a separation of zinc from iron, aluminum, chromium, manganese, and nickel, but not from cobalt unless, as Caldwell and Moyer[2] have shown, small concentrations of certain aldehydes, such as acrolein are present, which remove the hydrogen sulfide adsorbed on the surface of the zinc sulfide. These authors have also shown that the addition of 0.5 mg. of gelatin to 300 ml. of solution causes the zinc sulfide to coagulate immediately even in the cold. The proper *p*H may be obtained by the use of a buffer consisting of formic acid with ammonium formate. The addition of citric acid is advantageous when nickel, iron or manganese is present. Even more satisfactory is a buffer composed of sulfate and hydrosulfate.[3] The presence of chloride raises the *p*H required for the complete precipitation of zinc sulfide and is therefore, undesirable. The directions of Caldwell and Moyer,[4] using this buffer have been

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[1] Fales and Kenny, "Quantitative Analysis," Appleton-Century Co., 1939, Chap. XIII.

[2] Caldwell and Moyer, J. Am. Chem. Soc. **57**, 2372, 2375 (1935).

[3] Jeffreys and Swift, J. Am. Chem. Soc. **54**, 3219 (1932).

[4] *loc. cit.*

found convenient and accurate and are given here: Dilute the solution, free from chlorides, containing about 0.25 g. of zinc, and 6 to 8 g. of ammonium sulfate to 250-300 ml. and make it just acid to methyl orange. Pass a fairly rapid stream of hydrogen sulfide through the solution for 30 minutes at room temperature. Add 5 to 10 ml. of a 0.02 per cent solution of low ash gelatin with rapid stirring and allow the precipitate to settle. Let the solution stand 15 minutes, filter through a dense filter paper and wash with water, which, if iron is present, should contain a little hydrogen sulfide. The subsequent treatment depends upon the form in which the zinc is to be weighed. It may be converted by proper ignition to the oxide or sulfate, or it may be dissolved in hydrochloric acid, and, after the hydrogen sulfide has been boiled off, precipitated as zinc ammonium phosphate. If it is desired to filter the sulfide through a filtering crucible it is best to precipitate it hot, allow it to cool and to saturate the solution again at room temperature with hydrogen sulfide.

Errors in the Phosphate Method. Positive error: Abnormal composition of the precipitate, due to the presence of excessive amounts of ammonium salts in the solution or to the presence of sodium ion or potassium ion. Negative errors: 1. Incomplete precipitation due to the solution not being neutral; the addition of hydrogen sulfide to the filtrate and washings will cause the formation in a short time of a precipitate of zinc sulfide if precipitation was incomplete; 2. Loss during the washing process due to solubility; 3. Reduction of the precipitate during ignition.

Procedure. If the lead and copper have been separated electrolytically, the solution will now contain a considerable quantity of ammonium salts. It is desirable to remove them, as is done in limestone before the determination of magnesium, by oxidation to nitrous oxide and nitrogen with nitric and hydrochloric acids. To the filtrate from the hydrous ferric oxide, or, if no iron was present, to the solution from which the copper was removed, add 25 ml. of concentrated nitric acid and 25 ml. of concentrated hydrochloric acid, and evaporate the solution on the hot plate to dryness or to fumes of sulfur trioxide if much sulfuric acid is present. To the cool residue add a few ml. of concentrated hydrochloric acid, and warm the mixture for a few minutes. Dilute the solution to 50 ml., and when the salts have dissolved filter off any silica which may have separated, collecting the filtrate in a 400 ml. beaker.

If the lead was determined as lead sulfate, it will not be necessary to remove ammonium salts.

If the thiocyanate separation of copper was used, the ammonium salts were removed before the iron was separated. Or if no iron was present, the filtrate from the precipitate of cuprous thiocyanate may simply be concentrated to 175-200 ml.

Exactly neutralize the solution with ammonia, using methyl red or methyl orange as an indicator, and bring it to a volume of 175-200 ml. Heat the liquid to boiling and add slowly a clear solution of 6 grams of diammonium hydrogen phosphate in 35 ml. of water (Equation (9)). The first few drops of the phosphate will cause the indicator to turn red, due to the liberation of acid:

$$(11)\quad ZnCl_2 + (NH_4)_2HPO_4 = \downarrow ZnNH_4PO_4 + NH_4Cl + HCl.$$

Further addition of the phosphate will produce a yellow color in the solution, because of the formation of ammonium dihydrogen phosphate,

$$(12)\quad (NH_4)_2HPO_4 + HCl = NH_4H_2PO_4 + NH_4Cl$$

which, together with the excess of the diammonium hydrogen phosphate, acts as a buffer to maintain a neutral solution. A flocculent precipitate of zinc phosphate first forms; keep the solution hot (below boiling) until this substance changes to the crystalline zinc ammonium phosphate, which settles readily. Usually 15 to 30 minutes is required for this change. Let the precipitate stand for one hour without heating; then filter it through a Gooch or other filtering crucible, and wash it with cold water. Measure the volume of wash water used, and apply a correction of 0.5 mg. of zinc for each 100 ml. used, to cover the solubility loss. Continue the washing 10 or 12 times after the precipitate has been transferred to the crucible. Save the filtrate and washings in order to test them for complete precipitation. Dry the crucible in the oven for an hour; then place it inside another crucible to prevent access of flame gases, and heat it over the Meker burner, gradually at first to avoid loss due to sudden evolution of ammonia (Equation (10)). Ignite finally for half an hour at the full heat of the burner, with the crucible in a slanting position to give free access of air to the precipitate and thus avoid its reduction. Weigh the residue and repeat the ignitions until the weight is constant. Calculate the percentage of zinc from the weight of zinc pyrophosphate thus obtained. The conversion factor is 0.4290.

If a paper filter is used, great care must be taken to avoid reduction; the precipitate must be removed from the filter, and the latter must be burned separately. Such a method is not advisable.

Pass hydrogen sulfide for 5 minutes into the filtrate and washings from the zinc ammonium phosphate and let the solution stand for 1 hour. An opalescence that does not settle is probably free sulfur, especially if any sulfur dioxide was present. A light colored flocculent precipitate, which is zinc sulfide, is an indication that precipitation was incomplete, due to the fact that the solution was not exactly neutral. Filter this precipitate, using paper pulp if necessary, dissolve it in a little dilute hydrochloric acid, and boil off the hydrogen sulfide from the solution. Precipitate the zinc ammonium phosphate as directed above; keep the volume of the solution down to 30 or 40 ml., and add only 1 g. of the phosphate. The phosphate used must be the dibasic salt; if the monobasic salt is used, the solution will be acid. (How may the two salts be distinguished from each other?)

If the determination of zinc is ruined because of some accident, it is desirable in the second analysis to avoid the time required for the separation of the other metals. The following procedure, which has been found to give fairly good results in the presence of small amounts of tin or lead, and large amounts of copper, depends upon the use of the tartrate ion to prevent the precipitation of phosphates of these metals:

Dissolve a 1 g. sample of the brass in 30 ml. of 1 : 1 nitric acid, and exactly neutralize the solution with 1 : 5 ammonia. Use litmus paper as an indicator. Heat the solution nearly to boiling and add 25 g. of ammonium tartrate dissolved in 75 ml. of water and neutral to litmus. To the hot solution add slowly with constant stirring about 6 g. of diammonium hydrogen phosphate dissolved in 35 ml. of water. Keep the material hot for 1 hour, decant the supernatant liquid, and filter the precipitate through a paper filter. Wash it a few times with a 1 per cent ammonium tartrate solution. Dissolve the precipitate with hot, 1 : 3 nitric or hydrochloric acid, and wash the filter first with 1 per cent acid and finally with water. Neutralize the solution very carefully as before, add 15 g. of ammonium tartrate dissolved in 45 ml. of water, and reprecipitate the zinc ion with ammonium phosphate. Dissolve the precipitate and precipitate again. Filter the material through a filtering crucible, and wash it with water. Ignite the zinc ammonium phosphate to the pyrophosphate in the usual way. The neutralization is a very vital point in this method.

ANALYSIS OF A COPPER-NICKEL ALLOY

Coinage alloys of copper and nickel, monel metal, and other similar alloys contain in addition to the two principal metals a small amount of iron, but rarely more than traces of other elements. The electrolytic determination of copper in an acid solution serves as a separation of the copper from the iron and the nickel. After the removal of the small quantity of iron by repeated precipitations as the hydrous oxide, the nickel may be determined electrolytically from an ammoniacal solution. This separation of iron from nickel is not a perfect one, as has been mentioned on p. 348. With small amounts of iron it is satisfactory. The nickel remains in solution, probably as nickel-ammonia complex ion, $Ni(NH_3)_4^{++}$.

Procedure for Copper. If necessary, clean the alloy by washing it with ether, then with dilute ammonia followed by water, then with acetone, gently warming to remove any acetone. Weigh a 0.3-0.5 g. sample of the alloy into a beaker suitable for electrolytic work. Dissolve the sample in a mixture of 10 ml. of water, 1 ml. of concentrated sulfuric acid, and 2 ml. of concentrated nitric acid. Boil out the nitrous acid from the solution, and dilute it to 100 ml. The solution is ready for the deposition of copper either by the slow or rapid method described on pp. 431-432.

Wash the copper deposit very thoroughly with water by following the directions given under the determination of copper in brass, p. 445, and reserve the solution for the determination of iron and nickel. Dry and weigh the copper in the usual manner.

Procedure for Iron. Evaporate the solution containing the iron and nickel salts on a low temperature hot-plate (100-

110° C.) as far as possible, until the cover glass is dry—an indication that all nitrate ion has been removed. Nitrate ion, which may retard or make incomplete the deposition of the nickel, is removed at the point which proves most convenient. Ferrous iron is oxidized by the nitric acid during the evaporation. After cooling the residue, cautiously add water until the volume of the solution is 20-30 ml. Precipitate the small quantity of iron that is present by adding to the warm solution a liberal excess of ammonia (about 10 ml. of 6 *N* ammonia in excess). Filter the precipitate through a small paper, and receive the filtrate in an electrolytic type of beaker. Wash the precipitate three or four times with water. Place the original beaker under the filter; dissolve the precipitate in a little hot 6 *N* sulfuric acid, and wash the paper. Pour ammonia through the filter to precipitate the iron; use the same liberal excess of ammonia. Filter the precipitate, and collect the filtrate and washings in the electrolytic beaker containing the bulk of the nickel sulfate solution. Electrolyze this solution as described below. Ignite the hydrous ferric oxide to ferric oxide and weigh it. See p. 352.

Procedure for Nickel. The electrolytic deposition of nickel is a very satisfactory process, presumably because the complex ion, $Ni(NH_3)_4^{++}$, is partially broken down into the nickel ion and ammonia, and, as nickel ions are discharged and deposited, additional ones are rather slowly yielded by the ionization of the complex ions, so that a dense adherent layer of nickel is built up which is often almost indistinguishable from the platinum cathode. To the ammoniacal nickel solution add 15 ml. of concentrated ammonium hydroxide and dilute the solution to 100-150 ml. Carry out the electrolysis either by the slow or by the rapid method; use the current strengths that are recommended for the electrolysis of copper, p. 444. Wash and dry the deposit as directed for copper.

Report the percentages of copper, iron, and nickel, and their summation.

Remove the nickel deposit by dissolving it in concentrated nitric acid, free from chloride ion. A rather prolonged heating with the deposit covered by the acid will be found necessary. Wash the electrode with distilled water after the metal has been removed.

THE ANALYSIS OF GERMAN SILVER

Alloys of this type consist chiefly of copper, nickel and zinc, with a small amount of iron and often a little lead. Manganese and tin are occasionally found. The procedure provides for the determination of all of these elements. It is given in very brief outline, since the principles of the methods have already been described under the analysis of brass, pp. 434-456.

Procedure. Weigh a 0.5 g. sample of the alloy into a tall 150-200 ml. beaker. Cover the beaker and add slowly 10 ml. of concentrated nitric acid. When the action has almost ceased, warm the mixture on the hot-plate until solution is complete. Add 10 ml. of water and allow the solution to digest for 10-15 minutes.

Tin. If there is a white residue, it is stannic acid. It should be removed and be determined according to the procedure for tin in brass, p. 436.

Lead. Add 2 ml. of concentrated sulfuric acid to the filtrate from the stannic acid, or, if no tin is present, to the original solution. Evaporate the solution to remove all nitric acid. Do not evaporate to dryness. The salts should be slightly moist with concentrated sulfuric acid. Cool the residue, dilute the solution cautiously to 30-40 ml., stir thoroughly and allow it to stand for at least an hour to obtain complete precipitation of the lead sulfate. From this point, follow the procedure given for lead in brass, p. 439.

Copper. The filtrate from the lead sulfate, or the original solution if both tin and lead are absent, is used for the electrolytic determination of copper. Follow the procedure for the electrolytic determination of copper in brass, pp. 444-446. Note: If a deposit appears on the anode, it may be lead peroxide or manganese dioxide or a mixture of both. Dry and weigh it, and dissolve it in dilute nitric acid with the addition of a little pure hydrogen peroxide. After adding 1 ml. of dilute sulfuric acid, evaporate the solution to fumes; then dilute the cold residue, and after the salts have dissolved collect any insoluble lead sulfate. The manganese in the filtrate may be precipitated by adding ammonia slowly to the hot acid solution containing ammonium phosphate, until the solution is alkaline. The precipitate of manganese ammonium phosphate is filtered in a filtering crucible and washed with water. It is ignited, at first gently and then at the full heat of a burner of the Meker type. The manganese is weighed as the pyrophosphate.

Iron. To the solution from the copper determination add a few drops of pure hydrogen peroxide to re-oxidize the iron (electrolysis reduces it in part to the ferrous state), and then add a considerable excess of filtered, concentrated ammonia. Stir the solution thoroughly and heat to boiling. Filter off the hydrous ferric oxide and wash it with hot water. Dissolve in as little hot, dilute hydrochloric acid as possible, and receive the acid solution in a small separate beaker. Pour enough dilute ammonia through the filter to reprecipitate the iron. Heat the liquid to boiling, and filter and wash the precipitate. Add the filtrate and washings to the main solution containing the nickel and zinc. Ignite the precipitate and weigh the ferric oxide.

Nickel. Neutralize the combined filtrates from the determination of iron with hydrochloric acid and add 5 ml. of acid in excess. Add ammonium hydroxide slowly until the solution is faintly ammoniacal. During this neutralization process ammonium chloride is formed, which must be present to hold the zinc in solution. For each 0.1 g. of nickel that is expected to be present, add to the hot solution 0.5 g. of dimethylglyoxime dissolved in a little alcohol or acetone, and make sure that the solution is slightly ammoniacal. Let the beaker stand on the hot-plate for a few minutes, and test the solution for complete precipitation after the precipitate has coagulated. Allow the solution to cool by standing for an hour. Filter the precipitate on a weighed Gooch or other filtering crucible and wash it with hot water. Dry the nickel dimethlglyoxime in the oven at not over 110° C. and weigh. The precipitate contains 20.32 per cent of nickel. Too large an excess of reagent must be avoided as otherwise it, too, may be precipitated, since it is not very soluble in water.

Zinc. Acidify the filtrate from the determination of nickel with concentrated hydrochloric acid, and add 5 ml. of the concentrated acid in excess. Add 25 ml. of concentrated nitric acid to the solution and evaporate in a hood on the hot plate to dryness or to fumes of sulfur trioxide if much sulfuric acid is present. Organic matter and the large amount of ammonium salts are thus removed. To the cool residue add a few ml. of concentrated hydrochloric acid, warm the mixture for a few minutes, dilute to 50 ml., and, when the salts have dissolved, filter the solution if it is not perfectly clear. From this point follow the procedure for zinc in brass, pp. 453-455. The amount of diammonium hydrogen phosphate recommended for zinc in brass, 6 g., will be the correct amount to use in this case also. The zinc is finally weighed as the pyrophosphate.

THE ANALYSIS OF ALLOYS, SILICATES, ETC.

If the preceding work has been properly mastered, the analysis of the common alloys, silicates, and other chemical mixtures can be handled intelligently.

In the analysis of alloys it is first necessary to select a solvent in accordance with the principles that have just been outlined. After a solution is obtained which contains only a reasonable amount of free acid, the metals are separated in the usual order, which is almost the same as that followed in qualitative analysis. For the more common elements the order is (1) tin as stannic acid, (2) silver as silver chloride, (3) lead as lead sulfate or lead dioxide, (4) copper as copper or cuprous thiocyanate, (5) cadmium as cadmium sulfide from acid solution, (6) zinc as zinc sulfide from solution having *p*H 2, (7) iron and aluminum as basic acetates or benzoates or as hydrous oxides, (8) manganese as hydrous manganese dioxide or manganese sulfide, (9) calcium as calcium oxalate, (10) magnesium as magnesium ammonium phosphate.

The separation of arsenic, antimony, and tin is somewhat difficult and therefore has not been included. However, the student should be familiar with the methods for the determination of these elements. If elements of the zinc group are absent, iron, aluminum, and chromium may be separated from the metals in succeeding groups by an ordinary ammonia separation. After the heavy metals have been removed, nickel may be determined by titration with potassium cyanide. Nickel may be separated from nearly all other metals by precipitation from a slightly ammoniacal solution as nickel dimethylglyoxime, $NiC_8H_{14}N_4O_4$, which may be weighed as such or determined volumetrically. If metals precipitated by ammonia are present, citric or tartaric acid is first added to prevent their precipitation with the nickel dimethylglyoxime. Barium, strontium, and the alkalis are very seldom encountered in alloys.

Insoluble silicates must be decomposed by fusion with a base, preferably sodium carbonate unless an alkali metal is to be determined. After solution of the melt in dilute hydrochloric acid, silica is separated as already described, followed by the metals in the order given above. Ordinarily, silicates will not contain significant amounts of silver, arsenic, antimony, or tin. Lead, copper, and cadmium are occasionally found in silicates.

The analysis of complex sulfides is frequently required, since the heavy metals often occur in this form. The common solvent is either nitric acid or aqua regia. The metals are separated as usual in a sample which has been dissolved in acid but has not been fused. The sulfur is determined as already directed, and always on a separate sample. The metals in all ordinary, chemical mixtures are determined by similar methods.

Review Questions and Problems

1. Give each step in the complete analysis of an alloy of magnesium, silver, tin and cadmium. Give the formulas of the reagents added and of the products formed.

2. Give each step in the complete analysis of an alloy of zinc, antimony, iron and manganese.

3. Give each step in the complete analysis of a complex sulfide of nickel, arsenic, iron and zinc (5 determinations).

4. Give each step in the complete analysis of an insoluble silicate of manganese, lead, copper and calcium (5 determinations).

5. A neutral solution of lead perchlorate is electrolyzed, using platinum electrodes. What will be the products and in what relative amounts at each electrode? If considerable nitric acid is added to the solution what will be the products?

6. An acid solution of stannic chloride is precipitated by hydrogen sulfide. If fluoride is added, no precipitate is formed. If, now, gelatinous silica is added, stannic sulfide is precipitated. Explain these reactions.

7. A precipitate of stannic oxide from a sample weighing 1.0800 g. is reduced to metal in hydrogen and loses 0.1600 g. What percentage of tin is in the sample?

8. A sample of bronze contains 1.00 per cent of phosphorus. What error in the percentage of tin will be caused if it is assumed that the precipitate is pure stannic oxide instead of being contaminated with an amount of P_2O_5 equivalent to the phosphorus? *Ans.* 1.80 per cent high.

9. In problem 8 what would be the error if 1.00 per cent of antimony is present and is weighed with the stannic oxide as Sb_2O_4?

10. In a sample weighing 1.0770 g. the zinc is precipitated as sulfide and ignited to oxide, which weighed 0.5510 g. When this oxide was dissolved and tested with barium chloride 0.0720 g. of barium sulfate was obtained. What is the percentage of zinc in the sample?

11. How many ml. of 70.00 per cent nitric acid, sp. gr. 1.410 would theoretically be required to dissolve 10.000 g. of brass containing 38.00 per cent of zinc, 58.00 per cent of copper and 4.00 per cent of lead, assuming that the only reduction product is nitric oxide, NO?

12. Two g. of a mixture of red lead, Pb_3O_4, and litharge, PbO, was dissolved in perchloric acid containing 50.00 ml. of 0.1250 *N* oxalic acid. The excess of the latter required 15.50 ml. of 0.1200 *N* permanganate. Calculate the percentage of Pb_3O_4 in the sample. Ans. 75.25 per cent.

13. In a sample weighing 1.2500 g. the zinc was titrated with 45.00 ml. of potassium ferrocyanide of which 50.00 ml. required 45.00 ml. of 0.1100 *N* permanganate. Calculate the percentage of zinc in the sample.

14. The arsenic in a sample weighing 1.3500 g. was reduced to metal by stannous chloride and the metal was dissolved in 50.00 ml. of neutral 0.2150 *N* iodine. The excess of iodine required 10.50 ml. of 0.1050 *N* thiosulfate. Calculate the percentage of arsenic in the sample.

15. What weight of $CuSO_4 \cdot 5H_2O$ must be taken so that after the copper is deposited electrolytically and the solution is diluted to 500 ml. it will be exactly 0.05000 *N* in sulfuric acid?

16. A sample of an alloy weighing 0.9550 g. yielded 1.7550 g. of nickel dimethylglyoxime, 0.0575 g. of lead dioxide and 0.6230 g. of cupric oxide. Calculate the percentage of nickel, lead and copper in the alloy.

17. A sample of basic lead perchlorate weighing 1.0000 g. yields 1.0239 g. of lead sulfate; another sample of the same weight requires 40.88 ml. of 0.1100 *N* nitric acid to neutralize the hydroxide present. What is the formula for the salt? Ans. $Pb_3(OH)_4(ClO_4)_2$.

18. From 1.2500 g. of a material containing sodium chloride, sodium chlorate, sodium fluoride and inert material 1.4521 g. of silver chloride is obtained after reduction of the chlorate to chloride. For reduction of the chlorate, 38.68 ml. of 0.5100 *N* reducing agent is required. The total sodium is converted into sodium sulfate which weighs 1.2269 g. Calculate the percentage of each salt present. Ans. 32.00 per cent NaCl; 28.00 per cent $NaClO_3$; 24.00 per cent NaF.

19. The specific gravity of a lead-tin alloy is 8.85. Assuming that the metals alloy without change of volume, what is the percentage of each metal present? (Sp. gr. of lead 11.34, of tin, 6.54.)

20. From a sample of an alloy weighing 1.0650 g. 0.9075 g. of zinc pyrophosphate is obtained. It was later found that this precipitate contained manganese pyrophosphate equivalent to 0.0510 g. of manganese. Calculate the percentage of zinc in the alloy. What would have been the error in the determination of zinc if the presence of manganese had not been discovered?

CHAPTER XXI

COLORIMETRIC ANALYSIS

Theory and Principles. Colorimetric methods are particularly adapted to the rapid determination of very small amounts of material. For example, permanganate ion will impart a visible color to water in a concentration of 0.1 mg. per liter, an amount which could not be determined either gravimetrically or volumetrically. Colorimetric methods are not only rapid but they are, in general, easily carried out and, in many cases, with simple and inexpensive apparatus. Using visual methods of comparison the precision attainable is about 2 per cent, which is entirely satisfactory for the small amounts which are involved. In order that a colorimetric method may be successfully applied, two conditions must be fulfilled: 1. The substance must be intensely colored or it must be capable of being converted into a highly colored substance which bears a definite relation to the original material. 2. Colors developed by other substances must not be present except to a slight extent. Other relatively faint colors may be compensated by adding the same material to the standard. Colors of a different shade cannot be compared. Thus, an orange color cannot be compared with a yellow.

Colorimetry, as the term is commonly used by chemists, is a process of comparing the intensities of beams of light transmitted through solutions each of which contains the same colored material; the relative absorbing power of the solutions for light of course determines the amount transmitted. In practice each solution is illuminated by light of the same intensity from the same source, which may be either the sun or a suitable artificial source. The depth of the layer of liquid that is traversed by the light is varied for one or both solutions until the light of the same color and intensity reaches the eye, or a measuring device such as a photoelectric cell. Two laws are involved in making such comparisons: (1) *Lambert's law* (observed earlier by Bouguer also)[1] expresses the manner in which the intensity of the light transmitted, I_t, or the light absorbed, I_a, is related to the intensity of the incident light, I_0, and the *thickness, d, of the layer* traversed. Assume that the intensity of the light reflected is negligible, or canceled out by using two exactly similar vessels. Then $I_0 = I_a + I_t$. Now if A is the fraction of the incident light that is transmited by a layer of solution 1 cm. in depth, one form of the law is $I_t = I_0A^d$, or for the light absorbed, $I_a = I_0 - I_0A^d$. For a succession of layers of equal depth each layer absorbs the same fraction of the light that is incident to that layer, for any uniform colored medium; that is, the first layer absorbs 0.1 of the light incident to it, and each succeeding layer absorbs 0.1 of the light incident to it, etc. A more general form of the law derived from a simple differential equation is: $\log \frac{I_t}{I_0} = -kd$, the constant, k, being an absorption coefficient and the other terms as previously defined.

Beer's law is analogous to that of Lambert, but expresses the relation between light absorption, or transmission, and the *concentration* of the colored substance. Lambert's law is universally true but Beer's law is not strictly valid if the colored substance undergoes a change of degree of dissociation or association with change in concentration that is of such nature that the ratio of coloring power, or absorption, to concentration is variable. In a simple form the law may be written: $I_t = I_0A^c$ where c is the concentration of the colored substance and the other symbols are as previously defined. In a more general form the law may be expressed: $\log \frac{I_t}{I_0} = -k'c$.

If variations in both concentration and depth of layer traversed by the light are to be taken into account the laws apply simultaneously in the form: $\log \frac{I_t}{I_0} = -Kcd$, in which the value of the constant, K, called the extinction coefficient, will

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[1] Both Lambert's law and that of Beer are rigorously true only for light of a single wave-length. The use of a simple color filter to transmit light of a rather narrow band of wave-lengths adds to the specific nature of many colorimetric methods.

depend upon the units in which concentration and depth are expressed. If two different solutions of concentrations c_1 and c_2 of the same colored substance are illuminated with light of the same intensity from the same source, and if the depths traversed are respectively d_1 and d_2 at the point where both solutions transmit light of the same intensity, I_t, then: $\log \frac{I_t}{I_0} = -Kc_1d_1 = -Kc_2d_2$. That is $c_1d_1 = c_2d_2$, which is the simple basis of the methods that are considered in this chapter.[1]

Another type of colorimetry is involved in the colorimetric determination of *p*H as described on p. 133. In this case the intensities of color are not compared but the color of one solution is varied through the range of the indicator by varying the *p*H until the colors of the two solutions match.

Instruments for Comparing Colors. In colorimetry two methods are in use for the comparison of colors. In the simplest one the depth of the solution is kept constant and the concentration is varied. This is done by making up a series of standards of increasing concentration in tubes of exactly the same diameter, with plane glass bottoms. Such tubes are commonly called Nessler tubes. They are marked with a ring to indicate a definite volume, such as 50 ml. and they are supported in a rack so that a uniform light is reflected up through the bottom of the tubes by means of opal glass or a mirror covered with ground glass. See Fig. 61. The tube containing the unknown solution is compared with the series of standards by looking through the tubes placed side by side until one is found which matches it. The concentration of colored material in the unknown is then equal to the concentration in the standard comparison tube; or it may be between two of the standards, depending upon the interval between two standards. This method is particularly good for faint colors and is often more convenient for routine

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[1] The detailed mathematical treatment of the fundamental physical laws of colorimetry are given in the special treatises that are mentioned in the Appendix, p. 487. Fairly detailed treatments of chemical colorimetry and spectrophotometry are to be found in "Textbook of Inorganic Quantitative Analysis," Chap. XIV, by Kolthoff and Sandell; in "Inorganic Quantitative Analysis," Chap. XXV, by Fales and Kenny. The latter goes rather deeply into colorimetry as defined by the physicist. An excellent review of Spectrophotometric Methods in Analytical Chemistry is given by S. E. Q. Ashley, Ind. Eng. Chem. Anal. Ed. **11**, 72 (1939).

work where a series of permanent standards can be prepared. It also has the advantage that the apparatus required is simple and inexpensive.

In the other method of comparison the concentration is kept constant and the depth of the solution is varied until the intensity of the light appears the same in both solutions. This variation in depth of solutions is accomplished by having the light pass through transparent plungers dipping into the solutions. The cups containing the solution are attached to a scale and moved up and down until a match in color is obtained. The instrument used by chemists for this purpose is called a colorimeter, and the type most commonly used is the Duboscq colorimeter, as outlined in Fig. 62. To facilitate accurate comparison light passing through each tube passes through prisms before reaching the eye piece so that the field appears as a circle divided into halves separated by a faint line. The right half of the field is illuminated by the light passing through the left cup and vice versa. When a match has been obtained the concentrations of the coloring material are inversely proportional to the corresponding depths of the solutions. The colorimeter, although much more expensive than Nessler tubes, has the advantage that one standard will serve for a considerable number of unknown

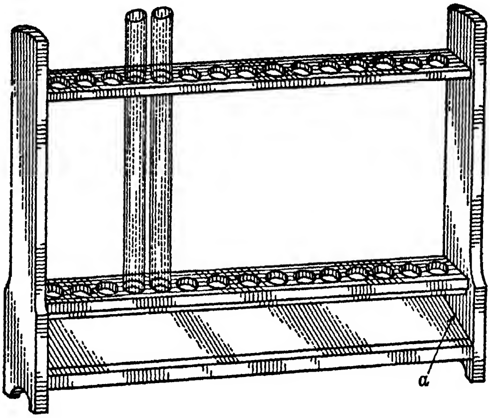

FIG. 61. Nessler Tubes and Rack. The white base slants up at an angle of 45° along the side, *a*, of the rack.

solutions, and a more accurate comparison of the colors can be made.

In all comparison methods it is essential that the illumination be uniform so that exactly the same intensity of light enters each of the solutions. The reflecting surface must therefore be clean and uniform. To prevent stray light from entering the solutions the colorimeter cups are usually made with black sides and clear bottoms. For very faintly colored solutions, longer tubes may be used.

Although there are no exceptions to Lambert's law, not all solutions obey Beer's law. The latter law holds over wide ranges for colored ions of strong electrolytes and for many organic compounds, but it is not valid for materials which ionize or associate or form complexes of different color with variation in concentration. This is of no consequence in the method which employs Nessler tubes, but in the use of a colorimeter such a deviation will introduce an error, the magnitude of which will increase with the difference in concentration between the standard and the solution being analyzed. It is, therefore, desirable to make up a standard which does not deviate too far from the concentration of the unknown solution.

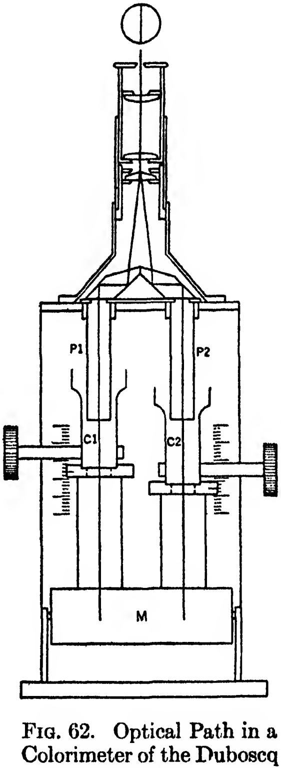

Fig. 62. Optical Path in a Colorimeter of the Duboscq Type.

P_1, P_2—plungers.
C_1, C_2—cups to hold the solutions.
M—mirror.

The two halves of the field viewed through the ocular appear equally bright when a match has been obtained.

In using a colorimeter, as with all optical instruments, the average of several readings should be taken. It should also be noted that after looking through the instrument for some time the eye becomes fatigued and is no longer able to distinguish small differences in intensity of color. This difficulty may be overcome by resting the eye between readings or by looking at some other object for a short time.

Very dilute suspensions of colored material may be used instead of true colored solutions providing they do not flocculate or settle out before the comparison is completed. Thus, a common colorimetric method for lead involves the comparison of suspensions of lead sulfide. In some cases a protective colloid such as gum arabic is added to prevent coagulation.

Turbidities may be compared in a similar way, part of the light being absorbed by the suspended material even though it is not colored. This is called the extinction or turbidimetric method. In the nephelometer the light reflected from the turbidity is the basis of comparison, and the light instead of passing up through the bottom of the tube strikes it at right angles to its axis. This nephelometric method has already been mentioned in connection with the "equal turbidity method" of determining the equivalence point in the titration of halide with silver ion (p. 174). By using a nephelometer to determine when the turbidities are equal, it is possible to detect an excess of silver or halide so slight that the method is sensitive enough to be used in atomic weight work. Moreover, if the turbidities are not equal it is possible from the readings to calculate the proper amount of silver or halide to be added.

Instead of comparing the color of two solutions visually instruments are now available in which this is done by means of photoelectric cells.[1] Such methods are capable of much greater precision than visual methods but the apparatus is relatively expensive.

Applications. Thousands of colorimetric methods have been published but many of them are not sufficiently reproducible to be satisfactory. Among the determinations frequently used may be mentioned that of manganese as permanganate, chromium as chromate or bichromate, iron as complex ferric thiocyanate or ferrous orthophenanthroline complex, ammonia as the compound formed with Nessler's reagent, silica as yellow silicomolyb-

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[1] This subject is admirably discussed by R. H. Müller, Ind. Eng. Chem., Anal. Ed. **11**, 1 (1939).

dic acid, titanium as yellow pertitanic acid and molybdenum as red complex thiocyanate.

Another application of colorimetry is the process termed colorimetric titration. In one cylinder or beaker is placed a definite volume of the solution to which has been added sufficient of the proper reagents to develop the full color of the material to be determined. In another similar vessel is placed slightly less than this volume of water containing the same amount of reagents. From a micro buret is added, with thorough stirring, a standard solution of the substance being determined until the color matches that of the solution to be analyzed. If the volumes of the two solutions do not differ by more than 2 per cent, no appreciable error will be introduced.

DETERMINATION OF MANGANESE IN STEEL

Principle. Manganese in concentrations not greater than 2 mg. per 100 ml. can readily be determined colorimetrically by first oxidizing it to permanganate. This is best accomplished by periodate in a sulfuric, phosphoric or perchloric acid solution: [1]

$$2Mn^{++} + 5IO_4^- + 3H_2O = 2MnO_4^- + 5IO_3^- + 6H^+.$$

Such a solution of permanganate is extremely stable. The only interfering metals are those which impart a color to the solution. The yellow color of ferric ion is removed by the addition of phosphoric acid, unless the amount of iron is greater than 0.5 g., in which case a slight color is noticeable. By varying the conditions the method may be applied to the determination of manganese in a large variety of materials.

Procedure. First make sure that the colorimeter is in satisfactory working order, and that its operation is understood. Remove both cups, fill them with water up to the shoulder, replace them in the instrument, and raise them by turning the milled head until the plungers dip under the surface of the water. Adjust the mirror so that maximum brilliancy is obtained and be sure that both halves of the field appear of equal brightness. Clean and dry the cups and plungers and replace the former in position. Raise them carefully until the plungers just touch the bottoms. Both scale readings should now be zero.

Dissolve 0.5-1.0 g. of steel in 50 ml. of dilute nitric acid

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[1] Willard and Greathouse, J. Am. Chem. Soc. 39, 2366 (1917).

(1 part of acid to 3 of water) in a 250 ml. conical flask and boil to expel oxides of nitrogen. Add 5-10 ml. of syrupy phosphoric acid, remove the burner, add, a little at a time, 1 g. of ammonium persulfate to oxidize the carbon always present in steel and boil for 10 minutes. Dilute with water to about 100 ml., add 0.4-0.5 g. of sodium or potassium periodate, or 0.5-0.6 g. of sodium paraperiodate, $Na_2H_3IO_6$, boil for 5 minutes, keep hot for 10 minutes, cool, dilute to 250 ml. in a volumetric flask and mix thoroughly. This solution should not contain more than 5.0 mg. of manganese.

Prepare a standard by dissolving a steel of known composition and oxidizing the manganese in the same way. If a standard steel is not available add sufficient standard permanganate solution to give about the same color to water containing the proper amount of nitric and phosphoric acids and ferric alum approximately equivalent to the iron present in the steel. Reduce the permanganate by the careful addition of dilute sodium nitrite to the warm solution, and oxidize the manganese by the addition of periodate as directed above. Be sure that the iron salt added is free from manganese by testing it with periodate, because many iron salts contain appreciable amounts. Chloride must be absent, and if present, it must be removed by evaporation with sulfuric acid.

Solutions prepared as directed are stable for two or three months if kept protected from dust, and a series of permanent standards may be prepared for use in Nessler tubes if desired.

Fill to the shoulder one cup of the colorimeter with the standard and the other with the solution to be analyzed. Be sure that the plungers dip below the surface and adjust the cup containing the standard to some convenient reading, such as 30 or 40 mm. While looking into the eyepiece adjust the other cup until the field appears uniform and take the reading. Rest the eye a moment and see if the two parts of the field still seem to be matched. Now approach the balance from the other direction and take another reading. Repeat the observation several times and average the readings. Calculate the concentration of unknown, x, reading a, from the concentration of the standard, c, and its reading, b:

$$\frac{x}{c} = \frac{b}{a}$$

Empty both cups and rinse them out thoroughly. Wash off each plunger with the stream from a wash bottle, holding a small beaker underneath. Dry it with a clean cloth, and wipe off carefully any drops of water on the instrument.

If a colorimeter is not available, a series of standards may be placed in Nessler tubes and the solution compared with these standards.

Review Questions and Problems

1. The manganese in a sample weighing 1.000 g. is oxidized to permanganate and diluted to 200 ml. The standard contains 2.0 mg. of manganese and is diluted to 250 ml. Readings, standard 25.1 mm.; unknown 30.5 mm. Calculate the percentage of manganese in the sample.

2. How much potassium periodate, KIO_4, is theoretically required to oxidize 0.100 g. of manganese to permanganate?

3. Calculate the error in per cent of manganese in problem 1 if an error of 1.0 mm. is made in reading the scale on the unknown solution.

4. In the colorimetric determination of manganese in steel the standard contains 1.10 ml. of 0.120 *N* permanganate in 100 ml. The solution of 2.000 g. of steel is diluted to 250 ml., and in 100 ml. of this the manganese is oxidized to permanganate, diluted to 500 ml. and the solutions compared in a colorimeter. Reading on standard 40.0 mm., on unknown 33 mm. Calculate the percentage of manganese in the steel.

APPENDIX

TABLE XXI. DISSOCIATION CONSTANTS OF SOME ACIDS AND BASES

(Reproduced with permission from Potentiometric Titrations,
I. M. Kolthoff and N. H. Furman, John Wiley & Sons, Inc., 2nd Ed., 1931.)

Acid	K_a	$p_K(= -\log K_a)$
Inorganic Acids		
Arsenious oxide	6×10^{-10}	9.22
Arsenic acid, first step	5×10^{-3}	2.30
Boric acid	6.6×10^{-10}	9.18
Carbonic acid, first step	3.04×10^{-7}	6.52
second step	4×10^{-11}	10.40
Phosphoric acid, first step	1.1×10^{-2}	1.96
second step	7.5×10^{-8}	7.13
third step	5×10^{-13}	12.30
Pyrophosphoric acid, first step	1.4×10^{-1}	0.85
second step	1.1×10^{-2}	1.96
third step	2.9×10^{-7}	6.54
fourth step	4×10^{-10}	9.40
Nitrous acid	4×10^{-4}	3.40
Sulfuric acid, second step	3×10^{-2}	1.50
Sulfurous acid, first step	1.7×10^{-2}	1.77
second step	1×10^{-7}	7
Hydrogen sulfide, first step	5.7×10^{-8}	7.24
second step	1.2×10^{-15}	14.92
Hydrocyanic acid	7.2×10^{-10}	9.14
Aliphatic Acids		
Acetic acid	1.75×10^{-5}	4.76
Citric acid, first step	8.2×10^{-4}	3.09
second step	1.77×10^{-5}	4.75
third step	3.9×10^{-7}	6.41
Formic acid	2×10^{-4}	3.7
Glycine	3.4×10^{-10}	9.47
Glycollic acid	1.52×10^{-4}	3.82
Hydrogen cyanide	7.2×10^{-10}	9.14
Lactic acid	1.55×10^{-4}	3.81
Oxalic acid, first step	3.8×10^{-2}	1.42
second step	6.1×10^{-5}	4.21
Succinic acid, first step	6.55×10^{-5}	4.18
second step	2.7×10^{-6}	5.57
Tartaric acid, first step	9.7×10^{-4}	3.01
second step	2.8×10^{-5}	4.55

TABLE XXI. DISSOCIATION CONSTANTS OF SOME ACIDS AND BASES—*Cont'd*

Acid	K_a	$p_K(= -\log K_a)$
Aromatic Acids		
Benzoic acid	6.86×10^{-5}	4.16
Phenol (carbolic acid)	1.3×10^{-10}	9.89
Phthalic acid, first step	1.26×10^{-3}	2.90
second step	3.9×10^{-6}	5.41
Picric acid	1.6×10^{-1}	0.80
Saccharin	2.5×10^{-2}	1.60
Salicylic acid	1.06×10^{-3}	2.97
Sulfanilic acid	6.3×10^{-4}	3.2

Inorganic Bases

Base	K_b	$p_K(= -\log K_b)$
Ammonia	1.75×10^{-5}	4.76
Hydrazine	3×10^{-6}	5.52
Organic Bases		
Aniline	3.5×10^{-10}	9.46
Ethylamine	5.6×10^{-4}	3.25
Diethylamine	1.26×10^{-3}	2.90
Triethylamine	6.4×10^{-4}	3.19
Glycine	2.7×10^{-12}	11.57

TABLE XXII. SOLUBILITY PRODUCTS OF SOME SALTS
(Averaged Values from the Literature)

(Reproduced with permission from Potentiometric Titrations, I. M. Kolthoff and N. H. Furman, John Wiley & Sons, Inc., 2nd Ed., 1931.)

Salt	S	p_s
Ag Salts		
Inorganic		
Silver		
bichromate	2×10^{-7}	6.7
bromide	4×10^{-13}	12.4
bromate	5×10^{-5}	4.3
carbonate	5×10^{-12}	11.3
chloride	1.1×10^{-10}	9.96
chromate	2×10^{-12}	11.7
cyanide	2×10^{-12}	11.7
hydroxide	2×10^{-8}	7.7
iodate	2×10^{-8}	7.7
iodide	1×10^{-16}	16
sulfide	1.6×10^{-49}	48.8
thiocyanate	1×10^{-12}	12
Organic		
Silver		
benzoate	9.3×10^{-5}	4.03
oxalate	5×10^{-12}	11.3
salicylate	1.4×10^{-5}	4.85
valerianate	8×10^{-5}	4.1
Ba Salts		
Barium		
carbonate	7×10^{-9}	8.16
chromate	2×10^{-10}	9.7
iodate	6×10^{-10}	9.22
sulfate	1×10^{-10}	10
Organic		
Barium		
Oxalate·$3\frac{1}{2}H_2O$	1.7×10^{-7}	6.77
Ca Salts		
Calcium		
carbonate	1.2×10^{-8}	7.92
fluoride	3.5×10^{-11}	10.46
iodate	6.5×10^{-7}	6.19
sulfate	6.1×10^{-5}	4.22
oxalate	2×10^{-9}	8.7
tartrate	7.7×10^{-7}	6.11

TABLE XXII. SOLUBILITY PRODUCTS OF SOME SALTS—*Continued*

(Averaged Values from the Literature)

Salt	S	p_s
Cd Salts		
Cadmium		
sulfide	4×10^{-29}	28.4
oxalate	1.1×10^{-8}	7.96
Ce Salts		
Cerium		
iodate	3.5×10^{-10}	9.46
oxalate	2.6×10^{-29}	28.39
tartrate	9.7×10^{-20}	19.01
Cu Salts		
Cuprous		
bromide	4.1×10^{-8}	7.39
chloride	1×10^{-6}	6
iodide	5×10^{-12}	11.3
sulfide	2×10^{-47}	46.7
thiocyanate	1.6×10^{-11}?	10.80?
Cupric		
iodate	1.4×10^{-7}	6.85
sulfide	8.5×10^{-45}	44.07
oxalate	2.9×10^{-8}	7.54
Fe Salts		
Ferrous		
hydroxide	3.2×10^{-14}	13.50
sulfide	3.7×10^{-19}	18.43
Hg Salts		
Mercurous		
bromide	1.3×10^{-21}	20.89
chloride	3.1×10^{-18}	17.5
iodide	1.2×10^{-28}	27.92
Mercuric		
oxide	1.4×10^{-26}	25.9
sulfide	4×10^{-53}	52.4
K Salts		
Potassium		
bitartrate	3×10^{-4}	3.5
La Salts		
Lanthanum		
iodate	5.9×10^{-10}	9.23
oxalate	2×10^{-28}	27.7
tartrate	2×10^{-19}	18.7

TABLE XXII. SOLUBILITY PRODUCTS OF SOME SALTS—*Continued*

(Averaged Values from the Literature)

Salt	S	p_s
Mg Salts		
Magnesium		
carbonate	2×10^{-4}	3.7
fluoride	7×10^{-9}	8.16
hydroxide	1.2×10^{-11}	10.92
ammonium phosphate	2.5×10^{-13}	12.6
oxalate	8.6×10^{-5}	4.07
Pb Salts		
Lead		
carbonate	3.3×10^{-14}	13.48
chromate	1.8×10^{-14}	13.75
fluoride	7×10^{-9}	8.16
iodate	1.2×10^{-13}	12.92
iodide	1.3×10^{-8}	7.5
sulfate	1×10^{-8}	8
sulfide	1×10^{-29}	29
oxalate	3.4×10^{-11}	10.47
Sr Salts		
Strontium		
carbonate	1.6×10^{-9}	8.80
sulfate	2.8×10^{-7}	6.56
oxalate	5×10^{-8}	7.3
Tl Salts		
Thallium		
bromide	2×10^{-6}	5.7
bromate	8.5×10^{-5}	4.07
chloride	1.5×10^{-4}	3.82
iodate	2.2×10^{-6}	5.66
iodide	2.8×10^{-8}	7.55
sulfide	4.5×10^{-23}	22.35

TABLE XXIII. SOME COMPLEX CONSTANTS

(Reproduced with permission from Potentiometric Titrations, I. M. Kolthoff and N. H. Furman, John Wiley & Sons, Inc., 2nd Ed., 1931)

Expression	Value of K	Expression	Value of K
$\frac{[Ag^+]\,[NH_3]^2}{[Ag(NH_3)_2{}^+]}$	6.8×10^{-8}	$\frac{[Hg^{++}]\,[Cl^-]^4}{[HgCl_4{}^-]}$	6×10^{-17}
$\frac{[Ag^+]\,[NO_2{}^-]^2}{[Ag(NO_2)_2{}^-]}$	1.5×10^{-3}	$\frac{[Hg^{++}]\,[Br^-]^4}{[HgBr_4{}^-]}$	2.2×10^{-22}
$\frac{[Ag^+]\,[S_2O_3{}^-]^2}{[Ag(S_2O_3)_2{}^=]}$	1×10^{-13}		
$\frac{[Ag^+]\,[CN^-]^2}{[Ag(CN)_2{}^-]}$	1×10^{-21}	$\frac{[Hg^{++}]\,[I^-]^4}{[HgI_4{}^-]}$	5×10^{-32}
$\frac{[Cu^+]\,[CN^-]^4}{[Cu(CN)^{4=}]}$	5×10^{-28}	$\frac{[Hg^{++}]\,[CN^-]^4}{[Hg[CN]_4{}^-]}$	4×10^{-42}
$\frac{[HgCl_2]\,[Cl^-]^2}{[HgCl_4{}^-]}$	1×10^{-2}	$\frac{[Hg^{++}]\,[CNS^-]^4}{[Hg(CNS)_4{}^-]}$	1×10^{-22}

STOCK SOLUTIONS OF ACID-BASE INDICATORS

Phenolphthalein. Dissolve 10 g. of the indicator in 600 ml. of 95 per cent alcohol and dilute to 1000 ml.

Methyl Red. Dissolve 2 g. of the indicator in 600 ml. of 95 per cent alcohol and dilute to 1000 ml.

Methyl Orange. Dissolve 1 g. of the indicator in water and dilute to 1000 ml.

Methyl Orange—Xylene Cyanole. Per a given weight of methyl orange add approximately 1.4 times as much xylene cyanole F.F. and dilute to a volume that will make the solution 0.1 per cent in methyl orange. Somewhat more or less of the xylene cyanole may need to be added and a test should be made using small weighed quantities of the two substances. The acidified indicator resembles permanganate solution; the neutral tint is gray or almost colorless and appears at *p*H 3.8. The alkaline color is green.[1]

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[1] K. C. D. Hickman and R. P. Linstead, J. Chem. Soc. (Lon.) **121**, 2502 (1922).

TABLE XXIV. FORMULAS FOR CALCULATING TITRATION DATA, *p*H VS. ML. OF REAGENT

1 Substance Titrated V_0 ml. of solution M_0 its molarity	2 Initial $[H^+]$ or $[OH^-]$	3 Intermediate Points 10, 50, 90, etc., per cent neutralized, V_1 ml. of reagent of M_1 molarity added	4 Equivalence Point	5 Excess of Reagent V_1 volume reagent M_1 its molarity V_T total volume
(1) Strong Acid........	$[H^+] = M_0$	$[H^+] = \frac{V_0M_0 - V_1M_1}{V_0+V_1}$	$\sqrt{K_w}$	$[OH^-] = \frac{V_1M_1}{V_T}$
(2) Strong Base.......	$[OH^-] = M_0$	$[OH^-] = \frac{V_0M_0 - V_1M_1}{V_0+V_1}$	$\sqrt{K_w}$	$[H^+] = \frac{V_1M_1}{V_T}$
(3) Weak Acid ($K_a = 10^{-5}$ to 10^{-8})	$[H^+] = \sqrt{M_0K_a}$	$[H^+] = \frac{[\text{Acid}]}{[\text{Salt}]}K_a$	$[OH^-] = \sqrt{\frac{K_w}{K_a}c}$	$[OH^-] = \frac{V_1M_1}{V_T}$ (Value in column 4 to be added)
(4) Weak Base ($K_b = 10^{-5}$ to 10^{-8})	$[OH^-] = \sqrt{M_0K_b}$	$[OH^-] = \frac{[\text{Base}]}{[\text{Salt}]}K_b$	$[H^+] = \sqrt{\frac{K_w}{K_b}c}$	$[H^+] = \frac{V_1M_1}{V_T}$ (Value in column 4 to be added)
(5) Salt of a Very Weak Acid (e.g. KCN)...	$[OH^-] = \sqrt{\frac{K_w}{K_a}c}$	$[H^+] = \frac{[\text{Acid}]}{[\text{Salt}]}K_a$	$[H^+] = \sqrt{[\text{Acid}]K_a}$	$[H^+] = \frac{V_1M_1}{V_T}$ (Correct for value in column 4)
(6) Salt of a Very Weak Base............	$[H^+] = \sqrt{\frac{K_w}{K_b}c}$	$[OH^-] = \frac{[\text{Base}]}{[\text{Salt}]}K_b$	$[OH^-] = \sqrt{[\text{Base}]K_b}$	$[OH^-] = \frac{V_1M_1}{V_T}$ (Add to $[OH^-]$ found in column 4)

THE LITERATURE OF ANALYTICAL CHEMISTRY

A search of the literature of chemistry for information about some special topic follows the same principles regardless of the topic. It is assumed that the student has received special instruction regarding the use of the library. If such instruction has not been received, it may be obtained by reading general guides to the literature of chemistry:

1. (A Guide to the) Literature of Chemistry, by E. J. Crane and A. M. Patterson, J. Wiley & Sons, Inc. 1927. Sec. 7, pp. 372-373, gives a classified list of analytical books.
2. Chemical Publications, by M. G. Mellon, McGraw-Hill Co. 1928.
3. Library Guide for the Chemist, by B. A. Soule, McGraw-Hill Co. 1938.

A. THE JOURNAL LITERATURE

Any fundamental search will go back to the original journal articles or other original sources. Abstract journals, notably Chemical Abstracts published by the American Chemical Society, from 1907 to date, with Decennial Indexes, are very important. Section seven of this journal, which appears twice a month, is devoted exclusively to brief reviews of analytical papers, books, patents, etc. Abstracts of methods dealing with special materials, e.g., foods, will be found in Section 12. Other similar journals, especially Chemisches Zentralblatt, 1830-date, should also be consulted.

The following list of journals, though not exhaustive, gives the principal ones that are devoted exclusively or nearly so to analytical papers:

The Analyst (London). 1877-date.
Annales de chimie analytique et de chimie appliquee et revue de chimie analytique reunis (Paris). 1896-date.
Industrial and Engineering Chemistry, Analytical Edition, 1930-date. (Easton, Pa.)

Journal of the Association of Official Agricultural Chemists. 1915-date.
Zeitschrift für analytische Chemie (Munich). 1862-date.

Other journals which carry a large proportion of analytical material are Mikrochemie; J. Research, National Bureau of Standards (Washington); Annales des falsifications et des fraudes; Zeitschrift für Untersuchung der Lebensmittel. Many analytical papers also appear in Am. Chem. J. (1879-1913); J. American Chemical Society; J. London Chemical Society; Trans. Society of Chemical Industry (London); Trans. Electrochem. Soc.; Berichte; J. prakt. Chemie; Zeitschrift für anorg. allgem. Chem.; also the journals of the chemical societies of various countries publish a considerable proportion of analytical papers. Periodical reviews of various fields, among them analytical, occur in Annual Reports of the Progress of Chemistry (London Chemical Society); in Chemical Reviews there are occasional analytical reviews; also in Ahren's Sammlung chemischer Vorträge.

For the convenience of the reader certain general and special treatises are classified in groups according to subject, in the following lettered divisions, with author, title, publisher and date of publication.

B. THEORY OF ANALYTICAL CHEMISTRY

H. Bassett. The Theory of Quantitative Analysis. Knopf, 1925.
N. Bjerrum. Die Theorie der alkalimetrischen und azidimetrischen Titrierungen. F. Enke, Stuttgart, 1914.
H. A. Fales and J. F. Kenny. Inorganic Quantitative Analysis. D. Appleton-Century Co., 1939.
M. Farnsworth. The Theory and Technique of Quantitative Analysis. J. Wiley & Sons, Inc., 1928.
L. P. Hammett. Solutions of Electrolytes. McGraw-Hill Co., 1936.
W. Ostwald. The Scientific Foundations of Analytical Chemistry. Translated by G. McGowan, Macmillan Co., 1908.
T. B. Smith. Analytical Processes, A Physico-Chemical Interpretation. Longmans, Green & Co., 1929.

J. Stieglitz. Qualitative Chemical Analysis, Volume I. Century Co., 1911.

J. H. Yoe. Chemical Principles. J. Wiley & Sons, 1937.

C. GENERAL TREATISES, Qualitative or Quantitative

H. Biltz and W. Biltz. Ausführung quantitativer Analysen. 2nd Ed. S. Hirzel, Leipzig, 1939.

A. Classen. Handbuch der analytischen Chemie. Enke, 1922.

F. Feigl. Qualitative Analyse mit Hilfe vom Tüpfelreaktionen. 3rd Ed. Akademische Verlagsgesellschaft, 1938. English Translation. Two volumes, Nordemann Publishing Co., 1937, 1940.

C. R. Fresenius. Qualitative Chemical Analysis. Translated by H. L. Wells. J. Wiley & Sons, Inc., 1908.

C. R. Fresenius. Quantitative Analysis, 2 Vols. Translated by A. I. Cohn. J. Wiley & Sons, Inc., 1908.

F. A. Gooch. Methods in Chemical Analysis. J. Wiley & Sons, Inc., 1929.

J. W. Mellor and H. V. Thompson. Quantitative Inorganic Analysis. 2nd Ed. Chas. Griffin, London, 1938.

W. F. Hillebrand and G. E. F. Lundell. Applied Inorganic Analysis. J. Wiley & Sons, Inc., 1929.

I. M. Kolthoff & E. B. Sandell. Textbook of Quantitative Inorganic Analysis. Macmillan Co., 1936.

G. E. F. Lundell and J. I. Hoffman. Outlines of Methods of Chemical Analysis. John Wiley & Sons, Inc., 1938.

B. M. Margosches. Die chemische Analyse. A series of monographs 1907-date, dealing with various general and special analytical topics. Edited by W. Böttger. Published by Enke.

A. D. Mitchell and A. M. Ward. Modern methods in Quantitative Chemical Analysis. Longmans, Green & Co., 1932.

A. A. Noyes. Qualitative Chemical Analysis. Macmillan Co., 9th Ed. 1923.

A. A. Noyes and W. C. Bray. Qualitative Analysis for the Rarer Elements. Macmillan Co., 1927.

R. K. McAlpine and B. A. Soule. Qualitative Chemical Analysis. D. Van Nostrand Co., 1933.

A. Rüdisüle. Nachweis, Bestimmung und Trennung der chemischen Elemente. Drechsel, 1912-1918.

F. P. Treadwell. Analytical Chemistry. Vol. I. Qualitative. 1921. Vol. II. Quantitative. 1919. Translated by W. T. Hall. J. Wiley & Sons, Inc.

W. D. Treadwell. Tabellen und Vorschriften zur Quantitativen Analyse. F. Deuticke, 1938.

GENERAL AND TECHNICAL

A. H. Allen. Commercial Organic Analysis. 10 Vols. 5th Ed. Blakiston, 1923-33.

American Society for Testing Materials, 230 South Broad St., Philadelphia, Pa. Publishes frequently revised standard methods for the analysis of Alloys, Cement, Coal, Coke, Oils, Rubber, etc. Individual methods, or assembled volumes of methods may be purchased.

E. Berl and G. Lunge. Chemischtechnische Untersuchungsmethode. 8th Ed. 5 Vols. Vol. I. Hirschwald; II-V. Springer. 1931-4.

R. C. Griffin. Technical Methods of Analysis. 2nd Ed. McGraw-Hill Co., 1921.

G. Lunge and C. A. Keane. Technical Methods of Chemical Analysis. 2nd Ed. 3 Vols. Edited by C. A. Keane and P. C. L. Thorne, D. Van Nostrand Co., 1924-1931.

Scott's Standard Methods of Chemical Analysis. 5th Ed. 2 Vols. Edited by N. H. Furman. D. Van Nostrand Co., 1939. Vol. I. Covers the analytical chemistry of the elements. Vol. II. Contains applied technical methods; also special techniques.

D. MICROCHEMISTRY AND MICROANALYSIS

A. A. Benedetti-Pichler and W. F. Spikes. Microtechnique of Inorganic Qualitative Analysis. Microchemical Service, 1935.

E. M. Chamot and C. W. Mason. Handbook of Chemical Microscopy. 2 Vols. Vol. I. 1938, 2nd Ed. Vol. II. 1930, 1st Ed.

See also Scott's Standard Methods, Vol. II.

F. Emich. Lehrbuch der Mikrochemie. Bergmann, 1926. Microchemical Laboratory Manual, Translated by F. Schneider, J. Wiley & Sons, Inc., 1932.

L. T. Hallett. Quantitative Microchemical Analysis. pp. 2460-2547, Vol. II of Scott's Standard Methods, 1939.

F. Pregl. Quantitative Organic Microanalysis. Translated by E. B. Daw. 3rd Ed. Churchill, 1937.

C. Weygand. Quantitative analytische Mikromethoden der organischen Chemie in vergleichender Darstellung. Akad. Verlagsgesellschaft, 1931.

SPECIALIZED TREATISES

Special Techniques and Special Substances

E. ELECTROANALYSIS (ELECTRODEPOSITION)

A. Classen and H. Danneel. Quantitative Analyse durch Elektrolyse. 7th Ed. Springer, 1927. The 5th Ed. by Classen and H. Cloeren, was translated by W. T. Hall, J. Wiley & Sons, Inc., 1919.

A. Fischer. Elektroanalytische Schnellmethoden. 2nd Ed. by A. Schleicher. Enke., 1926.

E. F. Smith. Electroanalysis. 4th Ed. Blakiston, 1907.

F. VOLUMETRIC ANALYSIS

H. Beckurts. Die Methoden der Massanalyse. 2nd Ed. Vieweg, 1931.

E. Brennecke, K. Fajans, N. H. Furman, R. Lang and H. Stamm. Newer Methods of Volumetric Analysis. Translated by R. E. Oesper. D. Van Nostrand Co., 1938.

A. Classen. Theorie und Praxis der Massanalyse. Akad. Verlagsgesellschaft, 1912.

G. S. Jamieson. Volumetric Iodate Methods. Chemical Catalog Co., 1926.

G. Jander and K. F. Jahr. Massanalyse. Theorie und Praxis der klassischen und der elektrochemischen Titrierverfahren. 2 Vols. de Gruyter & Co., 1935.

I. M. Kolthoff. Volumetric Analysis. 2 Vols. First Ed. translated by N. H. Furman. J. Wiley & Sons, Inc., 1928, 1929

Vol. I. covers Theoretical Principles. Vol. II. Practical Principles. 2nd Ed. Die Massanalyse, available in German. J. Springer, 1930, 1931.

E. Knecht and E. Hibbert. New Reduction Methods in Volumetric Analysis. Longmans, Green & Co., 1925. A specialized treatise upon the use of titanous solutions.

F. Sutton. Volumetric Analysis. 11th Ed. Revised by W. L. Sutton and A. E. Johnson. P. Blakiston's Son & Co., 1931.

ELECTROMETRIC METHODS

W. Böttger. Physikalische Methoden der analytischen Chemie, Part 3. Potentiometrische Massanalyse. Akademische Verlagsgesellschaft, Leipzig, 1939.

H. T. S. Britton. Conductometric Analysis. D. Van Nostrand Co., 1934.

W. Hiltner. Ausführung potentiometrischer Analysen. J. Springer, 1935.

G. Jander and O. Pfundt. Die visuelle Leitfähigkeitstitrationen. 2nd. Ed. F. Enke, 1934.

I. M. Kolthoff and N. H. Furman. Potentiometric Titrations. 2nd Ed. J. Wiley & Sons, Inc., 1931.

I. M. Kolthoff. Konduktometrische Titrationen. Steinkopf, 1923.

I. M. Kolthoff. *p*H and Electrotitrations. J. Wiley & Sons, Inc., 1931.

E. Müller. Die elektrometrische (potentiometrische) Massanalyse. 5th Ed. Steinkopf, 1932.

G. GAS ANALYSIS. (Also Fuel Analysis).

L. M. Dennis and M. H. Nichols. Gas Analysis. Revised Ed. Macmillan, 1929.

C. J. Engelder. Gas, Fuel and Oil Analysis. J. Wiley and Sons, Inc., 1931.

A. H. Gill. Gas Analysis. pp. 2336-2432, Vol. II. Scott's Standard Methods, 5th Ed., 1939.

G. Lunge. Technical Gas Analysis. Revised by H. R. Ambler. Gurney and Jackson, London, 1934.

S. W. Parr. Analysis of Fuel, Gas, Water and Lubricants. 4th Ed. McGraw-Hill Co., 1932.

A. H. White. Gas and Fuel Analysis. 2nd Ed. McGraw-Hill Co., 1920.

Winkler-Brunck. Lehrbuch der Technischen Gasanalyse. 5th Ed. Felix, 1927.

PHYSICO-CHEMICAL METHODS OF ANALYSIS

H. INSTRUMENTAL METHODS OF ANALYSIS. General.

W. N. Lacey. Instrumental Methods of Analysis. Macmillan, 1924.

G. F. Smith. Special and Instrumental Methods of Analysis. Edwards Bros., Ann Arbor, Mich., 1937.

I. CHROMATOGRAPHIC

L. Zechmeister. Die chromatographische Adsorptionsmethode. 2nd Ed. J. Springer, 1938.

J. THERMAL

H. A. Daynes. Gas Analysis by Measurement of Thermal Conductivity. Cambridge University Press, 1933.

P. E. Palmer and E. R. Weaver. Thermal Conductivity Method for the Analysis of Gases. Technologic Paper No. 249, National Bureau of Standards, 1924.

K. ELECTRICAL

(*a*) *Current-voltage Curves. Polarographic Method.*

J. Heyrovsky. Review of the polarographic field in Physikalische Methoden der chemischen Analyse, edited by W. Böttger. Akad. Verlagsgesellschaft, 1936.

H. Hohn. Chemische Analysen mit dem Polarographen. J. Springer, 1937.

I. M. Kolthoff and J. J. Lingane, Chem. Rev. 24, 1 (1939).

(*b*) *Radioactive Indicators.*

F. Paneth. Radio-elements as Indicators. McGraw-Hill, 1928.

(*c*) *Electrical Measurements* other than those above indicated or those used in titrations do not appear to have been collected in monographs. The effects: Conductance, Electromotive force; Magnetic susceptibility; Dielectric properties, and others are used in analysis.

L. OPTICAL METHODS

(1) **Emission Spectra.**

W. R. Brode. Chemical Spectroscopy. J. Wiley & Sons, Inc., 1939. See also Vol. II, p. 2592. Scott's Standard Methods, 1939.

W. Gerlach, ct al. Die chemische Emissions-Spektralanalyse. 3 Vols. Voss. 1929, 1933, 1936. Vols. I and II have been translated by A. Hilger Co., London.

G. Scheibe. Spektroskopische und radiometrische Analyse. Akad. Verlagsgesellschaft, 1933.

D. M. Smith. Metallurgical Analysis by the Spectrograph. Metals Research Assoc. (Brit.) Monograph 2, 1933.

Fluorescence.

J. A. Radley and J. Grant. Fluorescence Analysis in the Ultraviolet Light. 3rd Ed. D. Van Nostrand Co., 1939.

P. W. Danckwortt and J. Eisenbrand. Lumineszenz-Analyse in filtrierten ultravioletten Licht. 4th Ed. Akad. Verlagsgesellschaft, Leipzig, 1940.

(2) **Absorption of Radiation.**

(a) *Colorimetry.*

F. D. Snell and C. T. Snell. Colorimetric Methods of Analysis. D. Van Nostrand Co., 1936.

J. H. Yoe. Photometric Chemical Analysis. Vol. I. Colorimetry. J. Wiley & Sons, Inc., 1928.

(b) *Spectrophotometry.*

A. Hardy, et al. Handbook of Colorimetry. Technology Press, 1936.

C. Zeiss and W. Krebs. Klinische Kolorimetrie mit dem Pulfrich-Photometer. F. Volckmar, 1936.

(3) **X-ray Diffraction.**

G. L. Clark. Applied X-Rays. McGraw-Hill, 1927.

G. v. Hevesy. Chemical Analysis by X-Rays and its Applications. McGraw-Hill Co., 1932.

(4) **Reflection,** etc. *Nephelometry.*

J. H. Yoe. Photometric Analysis, Vol. II. J. Wiley & Sons, Inc., 1928.

(5) **Refraction.**

(a) *Refractometry.*

F. Löwe. Optische Messungen. 3rd Ed. Steinkopff, 1939.

W. A. Roth and F. Eisenlohr. Refraktometrisches Hilfsbuch. Veit, 1911.

(b) *Interferometry.*

J. D. Edwards. Application of the Interferometer to Gas Analysis. National Bur. of Standards Tech. Paper No. 131, 1919.

F. Löwe. See (a) above.

(6) **Optical Rotation.** *Polarimetry.*

C. A. Browne. Handbook of Sugar Analysis. J. Wiley & Sons, Inc., 1922.

H. Landholt. Optical Rotation of Organic Substances. 2nd Ed. The Chemical Publishing Co., 1902.

G. W. Rolfe. The Polariscope in the Chemical Laboratory. Macmillan Co., 1905.

U. S. Bureau of Standards Circular No. 44, Polarimetry. 2nd Ed., 1918.

M. INDICATORS; MEASUREMENT OF HYDROGEN-ION CONCENTRATION

H. T. S. Britton. Hydrogen Ions. D. Van Nostrand Co., 1929.

W. M. Clark. The Determination of Hydrogen Ions. 3rd Ed. Williams & Wilkins, 1928.

A. I. Cohn. Indicators and Test Papers. J. Wiley & Sons, Inc., 1909.

J. Grant. The Determination of Hydrogen-ion Concentration. Longmans, Green & Co., 1930.

I. M. Kolthoff. Acid-Base Indicators. Translated by C. Rosenblum. 4th Ed. The Macmillan Co., 1937.

L. Michaelis. Hydrogen-ion Concentration. Translated by W. A. Perlzweig. Williams and Wilkins, 1926.

N. THE ANALYSIS OF SPECIAL CLASSES OF SUBSTANCES

(1) **Agricultural Materials.**

R. E. Doolittle, et al. Official and Tentative Methods of Analysis. Assoc. of Official and Agr. Chemists. Washington, D. C. Revised every five years, 1935, 1940, etc.

H. W. Wiley. Principles and Practice of Agricultural Analysis. Chemical Publishing Co., 1926.

(2) **Foods.**

Doolittle, et al. Cited in sec. N (1).

M. B. Jacobs. Chemical Analysis of Foods and Food Products. Van Nostrand, 1938.

A. E. Leach and A. L. Winton. Food Inspection and Analysis. J. Wiley & Sons, Inc., 1924.

A. G. Woodman. Food Analysis. McGraw-Hill Co., 1924.

(3) **Iron, Steel and Related Materials.**

American Society for Testing Materials. Methods for the Chemical Analysis of Metals. Frequently revised.

W. Cartwright, T. W. Collier and A. Charlesworth. The Analysis of Non-Ferrous Metals and Alloys. Charles Griffin, 1937.

E. Gregory and W. W. Stevenson. Chemical Analysis of Metals and Alloys. Chemical Publishing Co., 1937.

F. Ibbotson. Chemical Analysis of Steelworks Materials. Longmans, Green & Co., 1920.

F. Ibbotson and L. Aitchison. The Analysis of Non-Ferrous Alloys. Longmans, Green and Co., 1915.

C. M. Johnson. Rapid Methods for the Chemical Analysis of Special Steels. 3rd Ed. J. Wiley & Sons, Inc., 1920.

N. W. Lord and D. J. Demorest. Metallurgical Analysis. 5th Ed. McGraw-Hill Co., 1924.

G. E. F. Lundell, J. I. Hoffman and H. A. Bright. Chemical Analysis of Iron and Steel. J. Wiley & Sons, Inc., 1932.

F. C. Phillips. Methods for the Chemical Analysis of Ores, Iron and Steel. Chemical Publishing Co., 1920.

W. W. Scott. Technical Methods of Metallurgical Analysis. D. Van Nostrand Co., 1923.

U. S. Steel Corporation, Carnegie Steel Co., Pittsburgh, Pa. Methods of the Chemists of the U. S. Steel Corporation: Methods for Sampling and Analysis of: Alloy Steels (1921); Ferroalloys and Bearing Metals (1921); separate treatises cover Pig Iron; Gases; Coal, Coke; Iron and Manganese Ores, etc.

(4) **Organic Substances.**

See Allen, under section C. See also section D on Microanalysis.

P. C. R. Kingscott and R. S. G. Knight. Quantitative Organic Analysis. Longmans, Green & Co., 1914.

(5) **Reagents.**

E. H. Archibald. Preparation of Pure Inorganic Substances. J. Wiley & Sons, Inc., 1932. This book gives atomic weight methods.

C. Krauch. Chemical Reagents. Scott, 1919.

J. Rosin. Standards and Tests for Reagent Chemicals. Based on the earlier treatise of B. L. Murray. D. Van Nostrand Co., 1937.

Organic Reagents for Inorganic Ions.

F. Feigl, treatise cited in section C.

Hopkin and Williams, Ltd. Organic Reagents for Metals. 3rd Ed., 1938.

Various makers of reagents [1] supply information on such reagents. Reviews with literature are to be found in certain elementary texts, such as those of Kolthoff and Sandell, Fales, etc., and in handbooks, section Q. Also in Scott's Standard Methods, Vol. I. 1939.

(6) **Rocks; Minerals and Ores.**

A. W. Groves. Silicate Analysis. London. 1937.

W. F. Hillebrand. Analysis of Silicate and Carbonate Rocks. Bulletin 700, U. S. Geological Survey. Government Printing Office, Washington, D. C. 1919.

A. H. Low. Technical Methods of Ore Analysis. 11th Ed. Revised by A. J. Weinig and W. P. Schroder. J. Wiley & Sons, Inc., 1939.

R. J. Meyer and O. Hauser. Die Analyse der seltenen Erden und der Erdsäuren. Enke, 1912.

R. B. Moore, et al. Analytical Methods for Certain Metals (includes Ce, Th, Mo, W, Ra, U, V, Ti and Zr). Bulletin 212, U. S. Bureau of Mines, Washington, 1923.

W. R. Schoeller and A. R. Powell. The Analysis of the Minerals and Ores of the Rarer Elements. Griffin & Co., 1919.

H. S. Washington. Manual of the Chemical Analysis of Rocks. 4th Ed. J. Wiley & Sons, Inc., 1930.

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[1] For example E. Merck, Darmstadt, publishes a booklet on organic reagents; The Eastman Kodak Co., Rochester, N. Y., publishes analytical procedures based upon organic reagents, as does also the G. F. Smith Chemical Co., Columbus, O.

(7) Water.

American Public Health Association. Standard Methods for the Examination of Water and Sewage. A. P. H. Assoc. New York, 1936. (Revised frequently.)

Chapters by D. K. French and by F. E. Hale, Scott's Standard Methods of Chemical Analysis, Vol. II, 1939.

W. P. Mason. Extermination of water. J. Wiley & Sons, Inc., 1917.

O. OTHER SOURCES OF ANALYTICAL METHODS

Many industries publish their analytical methods. Some of those of the U. S. Steel Corporation have been cited. Many other companies might be mentioned, as for example, the Aluminum Company of America, etc. Some federal bulletins and journals have been cited. The publications of the federal government may be purchased from the Superintendent of Documents, Washington, D. C. The Bureaus of Chemistry, Mines, Soils, Standards, the Public Health Service and others publish much valuable chemical investigation, including many analytical studies. Many of the modern descriptive bulletins issued by manufacturers of analytical instruments, reagents, or chemicals contain accurate scientific descriptions of analytical methods. The J. T. Baker Chemical Co. publishes a trade journal, The Chemist-Analyst, 1911-date. The text consists of analytical articles and laboratory suggestions. The above classes of literature are of course available in many countries. The scientific proceedings of various state societies contain analytical papers, e.g., Proc. Indiana State Acad. Sci., etc.

P. TABLES OF CONSTANTS

H. Landolt and R. Börnstein. Physikalisch-chemische Tabellen. Springer, 1923.

E. W. Washburn, et al. International Critical Tables. 7 Vols. McGraw-Hill Co.. 1926-1930.

Q. SMALL HANDBOOKS OF CONSTANTS; Chemical Calculations.

E. R. Caley. Analytical Factors and Their Logarithms. J. Wiley & Sons, Inc., 1932.

C. J. Engelder. Calculations of Quantitative Analysis. J. Wiley & Sons, Inc., 1939.

L. F. Hamilton and S. G. Simpson. Calculations of Quantitative Analysis. 3rd Ed. McGraw-Hill Co., 1939.

C. D. Hodgman. Handbook of Chemistry and Physics. Chemical Rubber Co. Revised annually.

G. W. C. Kaye and T. H. Laby. Tables of Physical and Chemical Constants. Longmans, Green & Co., 1926.

F. W. Küster. Logarithmische Rechentafeln für Chemiker. De Gruyter. Revised frequently.

N. A. Lange. Handbook of Chemistry. Handbook Publishing Co., Sandusky, O. Revised frequently.

E. H. Miller. The Calculations of Analytical Chemistry. Macmillan Co., 1921.

J. C. Olsen. Van Nostrand's Chemical Annual. McGraw-Hill Co., 1938.

QUADRATIC EQUATIONS. THE USE OF LOGARITHMS. EXPONENTIAL EXPRESSIONS

Quadratic Equations. In the calculations of analytical chemistry there are encountered certain problems in which the solution of a quadratic equation needs to be recalled, especially in certain types of problems involving ionization constants, solubility product constants, etc. All of the cases that arise may be reduced to the simple form:

$$x^2 + ax + b = 0.$$

The general solution of such an equation for x is:

$$x = -\tfrac{1}{2} a \pm \sqrt{(\tfrac{1}{2} a)^2 - b}.$$

Since a negative result would have no significance in a physical problem, the solution to be used here is

$$x = -\tfrac{1}{2} a + \sqrt{(\tfrac{1}{2} a)^2 - b}.$$

Illustration.—In calculations of the hydrogen ion concentration from the ionization constant of an acid at some particular concentration, an expression of the quadratic type may occur: Given the ionization constant of benzoic acid = $10^{-4.16}$, calculate the hydrogen ion concentration in a 0.1 molar solution of benzoic acid in water. Let x equal the hydrogen-ion concentration. Since equivalent amounts of hydrogen and benzoate ions are formed the concentration of the benzoate ion is also equal to x, and the benzoic acid concentration has been diminished from 0.1 to $0.1 - x$ due to the ionization. Therefore $\dfrac{x^2}{0.1 - x} = 10^{-4.16}$, or

$$x^2 + 10^{-4.16}\,x - 10^{-5.16} = 0.$$

$$x = -\tfrac{1}{2}\,10^{-4.16} + \sqrt{(\tfrac{1}{2}\,10^{-4.16})^2 + 10^{-5.16}}$$

$$= -\tfrac{1}{2}\,10^{-4.16} + \sqrt{\frac{10^{-8.32}\,(1 + 4 \times 10^{3.16})}{4}}$$

$$= 37.5 \times 10^{-4.16} = 10^{-2.586} \text{ or } p\text{H} = 2.586$$

The exact solution that has just been given differs so slightly from the easy approximate solution obtained by assuming that 0.1

may be used instead of 0.1 − x, that the simpler solution is frequently adequate: $\frac{x^2}{0.1} = 10^{-4.16}$; $x^2 = 10^{-5.16}$; $x = 10^{-2.58}$ or $p\text{H} = 2.58$. This simple approximation may always be tried, and if the value of x thus found is small compared with the value from which it is to be subtracted in the more exact formulation (in this case 0.1) the exact calculation need not be made.

Quadratic equations arise in solubility product calculations in the following manner: Suppose that 500 ml. of 0.001 *M* ammonium sulfate is saturated with barium sulfate by shaking with an excess of solid barium sulfate. If the solubility product of barium sulfate is 10^{-10}, how much barium sulfate is dissolved? Assuming that the ammonium sulfate is completely ionized, the concentration of the sulfate ion is equal to 0.001 plus x, where x is the molar concentration of sulfate that is introduced by the small amount of barium sulfate that dissolves, and the concentration of the barium ion is also x. Then

$$[\text{Ba}^{++}]\,[\text{SO}_4^{=}] = 10^{-10}$$

$$x\,(0.001 + x) = 10^{-10},$$

or $x^2 + 0.001\,x - 10^{-10} = 0.$

$$x = -\tfrac{1}{2}\,10^{-3} + \sqrt{(\tfrac{1}{2}\,10^{-3})^2 + 10^{-10}}$$

$$x = 0.0001 \times 10^{-3} = 10^{-7}$$

moles of BaSO_4 per liter or

$$\tfrac{1}{2} \times 10^{-7} \times 233 = 1.17 \times 10^{-5} \text{ g. per 500 ml.}$$

Logarithms. The use of logarithms, and of the slide-rule as well, involves primarily a knowledge of the rules of transformations involving exponents. Common or Briggsian logarithms are exponents to which the number 10 must be raised to give the numbers in question. For example, the logarithm of 1000 is 3 for $10^3 = 1000$. After transforming all of the numbers to 10 with a proper exponent, as for example $10^{-2.34567}$, $10^{-2.00000}$, etc., multiplications are made by adding the exponents, divisions by subtracting exponents. If a slide-rule is to be used, numbers are set down on scales at logarithmic intervals. By moving the slide of the rule multiplications may be made by adding distances of slide against rule, or divisions by subtracting distances, without looking up the actual logarithms, since the distances ruled on the two parts of the instrument have the numbers set down upon them at distances proportional to their respective logarithms, i.e., 1 opposite the origin or zero, ten opposite a distance of 1.0000 and intervening numbers 2 at 0.3010, 3 at 0.4771, 4 at 0.6021 of the distance from 0 to 10 on the number scale.

In a table of logarithms there are set down *mantissas* without consideration of order of magnitude of the number. For example, the same mantissa would be set down for any of the quantities 0.003, or 0.03, 0.3, 3., 30, 300, etc. We then need another number to show order of magnitude; this number is the *characteristic.* If we rewrite the above expressions 0.003, etc., as respectively 3×10^{-3}, 3×10^{-2}, 3×10^{-1}, 3×10^{0}, 3×10^{1}, 3×10^{2} we see that we handle the order of magnitude by considering the number in any case as a product of some small number times 10 raised to an appropriate power. The logarithm of 3 is 0.4771; the logarithm of 10 to any power is the exponent indicated for the 10. For 3×10^{-3} we then have the logarithm $-3.$ plus 0.4771. This could be written -2.5229 or alternatively in the form $7.4771 - 10$. The latter form is very convenient, as will be indicated later.

In general, then if we desire to multiply the numbers N_1, N_2, N_3 and divide by another, N_4 to find the result, N_5, the process is as follows:

$$\begin{aligned} \text{Log } N_1 &= a & N_1 &= 10^a \\ \text{Log } N_2 &= b & N_2 &= 10^b \\ \text{Log } N_3 &= c & N_3 &= 10^c \\ \text{Log } N_4 &= d & N_4 &= 10^d \end{aligned}$$

N_5 to be determined.

$$\frac{N_1 \times N_2 \times N_3}{N_4} = N_5 = \frac{10^a \times 10^b \times 10^c}{10^d} = 10^{a+b+c-d}$$

Hence the logarithm of $N_5 = a + b + c - d$. We then find from the table the number corresponding to this logarithm.

Illustration.—The following type of operation is frequently encountered in analysis:

To find the result of $\dfrac{0.7564 \times 0.2474 \times 100}{0.3423}$

$$\begin{array}{lll}
 & \log 0.7564 & = 9.87875 - 10 \\
\text{Add} & \log 0.2474 & = 9.39340 - 10 \\
 & \log 100 & = 2.00000 \\
\hline
 & \text{Sum} & 11.27115 - 10 \\
\text{Subtr.} & \log 0.3423 & = 9.53441 - 10 \\
\hline
 & \text{log result} & 1.73674
\end{array}$$

Result: 54.54 (the logarithm is nearer that of 54.54 than of 54.55)

The characteristic of 1. in the logarithm indicates that the number lies between 10 and 99.9999 . . . , because the logarithm of 10 is 1 and that of 100 is 2. hence any logarithm between 1 and 2 denotes a number greater than 10 and less than 100. For numbers greater than 1 the characteristic of the logarithm is one less than the number of figures to the left of the decimal point. For example for the numbers 6666, 666.6, 66.66 and 6.666 the characteristics are respectively 3, 2, 1, and 0, while the mantissas are in each case the same, namely 0.82387. For quantities less than 1, for example 0.6666, 0.06666, 0.006666, etc., the characteristics are -1, -2, -3, etc., while the mantissas are in all of the cases 0.82387. There is no confusion when both characteristic and mantissa are positive; when the characteristic is negative, for example for 0.06666, with a characteristic of -2, we should recall that the logarithm is the algebraic sum of -2 and 0.82387, which is -1.17613 or may be written $8.82387 - 10$. In certain books and tables the log of 0.06666 might be written: $\bar{2}.82387$, the minus sign above the 2 indicating that it is negative and the rest of the expression positive.

Exponential expressions. The handling of very small constants and small quantities in general is mathematically simplified if we convert numbers to the form 10^x where x is an appropriate exponent. There is frequent occasion to make such transformations in dealing with hydrogen-ion concentrations, equilibrium constants, etc. Some examples of the types of transformation that is common are the following: To convert 0.00046 to the form of 10 raised to the proper power. 0.00046 is the same as 4.6 divided by 10^4, which is identical with 4.6×10^{-4}. Now convert 4.6 to the proper form by looking up the log of 4.6 which is 0.66. Hence $4.6 = 10^{0.66}$. Then $0.00046 = 10^{0.66} \times 10^{-4} = 10^{-3.34}$. This number is $10^{(\log 0.00046)}$. Conversely, if a calculation gives a result $10^{-7.24}$; this may be desired in the form: small number $\times 10^{-x}$. To make the transformation we have $10^{0.76} \times 10^{-8}$ and $10^{0.76}$ is the number whose log is $0.76 = 5.8$. Therefore $10^{-7.24} = 5.8 \times 10^{-8} = 0.000000058$. The principle of significant figures is followed in the transformations.

The expression of small quantities in the form of 10^x and the use of the transformations that have been described are frequently useful in calculations involving hydrogen-ion concentrations and *p*H, Chapter VII, and in connection with solubility products, Chapters IX and XV, and oxidation-reduction equilibria, Chapter X. Numerous applications of the principles will be found in these chapters.

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
100	00 000	043	087	130	173	217	260	303	346	380
01	432	475	518	561	604	647	689	732	775	817
02	860	903	945	988	*030	*072	*115	*157	*199	*242
03	01 284	326	368	410	452	494	536	578	620	662
04	703	745	787	828	870	912	953	995	*036	*078
05	02 119	160	202	243	284	325	366	407	449	490
06	531	572	612	653	694	735	776	816	857	898
07	938	979	*019	*060	*100	*141	*181	*222	*262	*302
08	03 342	383	423	463	503	543	583	623	663	703
09	743	782	822	862	902	941	981	*021	*060	*100
110	04 139	179	218	258	297	336	376	415	454	493
11	532	571	610	650	639	727	706	805	844	883
12	922	961	999	*038	*077	*115	*154	*192	*231	*269
13	05 308	346	385	423	461	500	538	576	614	652
14	690	729	767	805	843	881	918	956	994	*032
15	06 070	108	145	183	221	258	296	333	371	408
16	446	483	521	558	595	633	670	707	744	781
17	819	856	893	930	967	*004	*041	*078	*115	*151
18	07 188	225	262	298	335	372	408	445	482	518
19	555	591	628	664	700	737	773	809	846	882
120	918	954	990	*027	*063	*099	*135	*171	*207	*243
21	08 279	314	350	386	422	458	493	529	565	600
22	636	672	707	743	778	814	849	884	920	955
23	991	*026	*061	*096	*132	*167	*202	*237	*272	*307
24	09 342	377	412	447	482	517	552	587	621	656
25	691	726	760	795	830	864	899	934	968	*003
26	10 037	072	106	140	175	209	243	278	312	346
27	380	415	449	483	517	551	585	619	653	687
28	721	755	789	823	857	890	924	958	992	*025
29	11 059	093	126	160	193	227	261	294	327	361
130	394	428	461	494	528	561	594	628	661	694
31	727	760	793	826	860	893	926	959	992	*024
32	12 057	090	123	156	189	222	254	287	320	352
33	385	418	450	483	516	548	581	613	646	678
34	710	743	775	808	840	872	905	937	969	*001
35	13 033	066	098	130	162	194	226	258	290	322
36	354	386	418	450	481	513	545	577	609	640
37	672	704	735	767	799	830	862	893	925	956
38	988	*019	*051	*082	*114	*145	*176	*208	*239	*270
39	14 301	333	364	395	426	457	489	520	551	582
140	613	644	675	706	737	768	799	829	860	891
41	922	953	983	*014	*045	*076	*106	*137	*168	*198
42	15 229	259	290	320	351	381	412	442	473	503
43	534	564	594	625	655	685	715	746	776	806
44	836	866	897	927	957	987	*017	*047	*077	*107
45	16 137	167	197	227	256	286	316	346	376	406
46	435	465	495	524	554	584	613	643	673	702
47	732	761	791	820	850	879	909	938	967	997
48	17 026	056	085	114	143	173	202	231	260	289
49	319	348	377	406	435	464	493	522	551	580
150	609	638	667	696	725	754	782	811	840	869
N	0	1	2	3	4	5	6	7	8	9

PP

	44	43	42
1	4.4	4.3	4.2
2	8.8	8.6	8.4
3	13.2	12.9	12.6
4	17.6	17.2	16.8
5	22.0	21.5	21.0
6	26.4	25.8	25.2
7	30.8	30.1	29.4
8	35.2	34.4	33.6
9	39.6	38.7	37.8

	41	40	39
1	4.1	4.0	3.9
2	8.2	8.0	7.8
3	12.3	12.0	11.7
4	16.4	16.0	15.6
5	20.5	20.0	19.5
6	24.6	24.0	23.4
7	28.7	28.0	27.3
8	32.8	32.0	31.2
9	36.9	36.0	35.1

	38	37	36
1	3.8	3.7	3.6
2	7.6	7.4	7.2
3	11.4	11.1	10.8
4	15.2	14.8	14.4
5	19.0	18.5	18.0
6	22.8	22.2	21.6
7	26.6	25.9	25.2
8	30.4	29.6	28.8
9	34.2	33.3	32.4

	35	34	33
1	3.5	3.4	3.3
2	7.0	6.8	6.6
3	10.5	10.2	9.9
4	14.0	13.6	13.2
5	17.5	17.0	16.5
6	21.0	20.4	19.8
7	24.5	23.8	23.1
8	28.0	27.2	26.4
9	31.5	30.6	29.7

	32	31	30
1	3.2	3.1	3.0
2	6.4	6.2	6.0
3	9.6	9.3	9.0
4	12.8	12.4	12.0
5	16.0	15.5	15.0
6	19.2	18.6	18.0
7	22.4	21.7	21.0
8	25.6	24.8	24.0
9	28.8	27.9	27.0

PP

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
150	17 609	638	667	696	725	754	782	811	840	869
51	898	926	955	984	*013	*041	*070	*099	*127	*156
52	18 184	213	241	270	298	327	355	384	412	441
53	469	498	526	554	583	611	639	667	696	724
54	752	780	808	837	865	893	921	949	977	*005
55	19 033	061	089	117	145	173	201	229	257	285
56	312	340	368	396	424	451	479	507	535	562
57	590	618	645	673	700	728	756	783	811	838
58	866	893	921	948	976	*003	*030	*058	*085	*112
59	20 140	167	194	222	249	276	303	330	358	385
160	412	439	466	493	520	548	575	602	629	656
61	683	710	737	763	790	817	844	871	898	925
62	952	978	*005	*032	*059	*085	*112	*139	*165	*192
63	21 219	245	272	299	325	352	378	405	431	458
64	484	511	537	564	590	617	643	669	696	722
65	748	775	801	827	854	880	906	932	958	985
66	22 011	037	063	089	115	141	167	194	220	246
67	272	298	324	350	376	401	427	453	479	505
68	531	557	583	608	634	660	686	712	737	763
69	789	814	840	866	891	917	943	968	994	*019
170	23 045	070	096	121	147	172	198	223	249	274
71	300	325	350	376	401	426	452	477	502	528
72	553	578	603	629	654	679	704	729	754	779
73	805	830	855	880	905	930	955	980	*005	*030
74	24 055	080	105	130	155	180	204	229	254	279
75	304	329	353	378	403	428	452	477	502	527
76	551	576	601	625	650	674	699	724	748	773
77	797	822	846	871	895	920	944	969	993	*018
78	25 042	066	091	115	139	164	188	212	237	261
79	285	310	334	358	382	406	431	455	479	503
180	527	551	575	600	624	648	672	696	720	744
81	768	792	816	840	864	888	912	935	959	983
82	26 007	031	055	079	102	126	150	174	198	221
83	245	269	293	316	340	364	387	411	435	458
84	482	505	529	553	576	600	623	647	670	694
85	717	741	764	788	811	834	858	881	905	928
86	951	975	998	*021	*045	*068	*091	*114	*138	*161
87	27 184	207	231	254	277	300	323	346	370	393
88	416	439	462	485	508	531	554	577	600	623
89	646	669	692	715	738	761	784	807	830	852
190	875	898	921	944	967	989	*012	*035	*058	*081
91	28 103	126	149	171	194	217	240	262	285	307
92	330	353	375	398	421	443	466	488	511	533
93	556	578	601	623	646	668	691	713	735	758
94	780	803	825	847	870	892	914	937	959	981
95	29 003	026	048	070	092	115	137	159	181	203
96	226	248	270	292	314	336	358	380	403	425
97	447	469	491	513	535	557	579	601	623	645
98	667	688	710	732	754	776	798	820	842	863
99	885	907	929	951	973	994	*016	*038	*060	*081
200	30 103	125	146	168	190	211	233	255	276	298
N	0	1	2	3	4	5	6	7	8	9

PP

	29	28
1	2.9	2.8
2	5.8	5.6
3	8.7	8.4
4	11.6	11.2
5	14.5	14.0
6	17.4	16.8
7	20.3	19.6
8	23.2	22.4
9	26.1	25.2

	27	26
1	2.7	2.6
2	5.4	5.2
3	8.1	7.8
4	10.8	10.4
5	13.5	13.0
6	16.2	15.6
7	18.9	18.2
8	21.6	20.8
9	24.3	23.4

	25
1	2.5
2	5.0
3	7.5
4	10.0
5	12.5
6	15.0
7	17.5
8	20.0
9	22.5

	24	23
1	2.4	2.3
2	4.8	4.6
3	7.2	6.9
4	9.6	9.2
5	12.0	11.5
6	14.4	13.8
7	16.8	16.1
8	19.2	18.4
9	21.6	20.7

	22	21
1	2.2	2.1
2	4.4	4.2
3	6.6	6.3
4	8.8	8.4
5	11.0	10.5
6	13.2	12.6
7	15.4	14.7
8	17.6	16.8
9	19.8	18.9

PP

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9	PP
200	30 103	125	146	168	190	211	233	255	276	298	
01	320	341	363	384	406	428	449	471	492	514	
02	535	557	578	600	621	643	664	685	707	728	
03	750	771	792	814	835	856	878	899	920	942	
04	963	984	*006	*027	*048	*069	*091	*112	*133	*154	
05	31 175	197	218	239	260	281	302	323	345	366	
06	387	408	429	450	471	492	513	534	555	576	
07	597	618	639	660	681	702	723	744	765	785	
08	806	827	848	869	890	911	931	952	973	994	
09	32 015	035	056	077	098	118	139	160	181	201	
210	222	243	263	284	305	325	346	366	387	408	
11	428	449	469	490	510	531	552	572	593	613	
12	634	654	675	695	715	736	756	777	797	818	
13	838	858	879	899	919	940	960	980	*001	*021	
14	33 041	062	082	102	122	143	163	183	203	224	
15	244	264	284	304	325	345	365	385	405	425	
16	445	465	486	506	526	546	566	586	606	626	
17	646	666	686	706	726	746	766	786	806	826	
18	846	866	885	905	925	945	965	985	*005	*025	
19	34 044	064	084	104	124	143	163	183	203	223	
220	242	262	282	301	321	341	361	380	400	420	
21	439	459	479	498	518	537	557	577	596	616	
22	635	655	674	694	713	733	753	772	792	811	
23	830	850	869	889	908	928	947	967	986	*005	
24	35 025	044	064	083	102	122	141	160	180	199	
25	218	238	257	276	295	315	334	353	372	392	
26	411	430	449	468	488	507	526	545	564	583	
27	603	622	641	660	679	698	717	736	755	774	
28	793	813	832	851	870	889	908	927	946	965	
29	984	*003	*021	*040	*059	*078	*097	*116	*135	*154	
230	36 173	192	211	229	248	267	286	305	324	342	
31	361	380	399	418	436	455	474	493	511	530	
32	549	568	586	605	624	642	661	680	698	717	
33	736	754	773	791	810	829	847	866	884	903	
34	922	940	959	977	996	*014	*033	*051	*070	*088	
35	37 107	125	144	162	181	199	218	236	254	273	
36	291	310	328	346	365	383	401	420	438	457	
37	475	493	511	530	548	566	585	603	621	639	
38	658	676	694	712	731	749	767	785	803	822	
39	840	858	876	894	912	931	949	967	985	*003	
240	38 021	039	057	075	093	112	130	148	166	184	
41	202	220	238	256	274	292	310	328	346	364	
42	382	399	417	435	453	471	489	507	525	543	
43	561	578	596	614	632	650	668	686	703	721	
44	739	757	775	792	810	828	846	863	881	899	
45	917	934	952	970	987	*005	*023	*041	*058	*076	
46	39 094	111	129	146	164	182	199	217	235	252	
47	270	287	305	322	340	358	375	393	410	428	
48	445	463	480	498	515	533	550	568	585	602	
49	620	637	655	672	690	707	724	742	759	777	
250	794	811	829	846	863	881	898	915	933	950	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**PP**

	22	21
1	2.2	2.1
2	4.4	4.2
3	6.6	6.3
4	8.8	8.4
5	11.0	10.5
6	13.2	12.6
7	15.4	14.7
8	17.6	16.8
9	19.8	18.9

	20
1	2.0
2	4.0
3	6.0
4	8.0
5	10.0
6	12.0
7	14.0
8	16.0
9	18.0

	19
1	1.9
2	3.8
3	5.7
4	7 6
5	9 5
6	11.4
7	13.3
8	15.2
9	17.1

	18
1	1.8
2	3.6
3	5.4
4	7.2
5	9.0
6	10.8
7	12.6
8	14.4
9	16.2

	17
1	1.7
2	3.4
3	5 1
4	6.8
5	8.5
6	10.2
7	11 9
8	13.6
9	15.3

TABLE I.—COMMON LOGARITHMS OF NUMBERS
To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
250	39 794	811	829	846	863	881	898	915	933	950
51	967	985	*002	*019	*037	*054	*071	*088	*106	*123
52	40 140	157	175	192	209	226	243	261	278	295
53	312	329	346	364	381	398	415	432	449	466
54	483	500	518	535	552	569	586	603	620	637
55	654	671	688	705	722	739	756	773	790	807
56	824	841	858	875	892	909	926	943	960	976
57	993	*010	*027	*044	*061	*078	*095	*111	*128	*145
58	41 162	179	196	212	229	246	263	280	296	313
59	330	347	363	380	397	414	430	447	464	481
260	497	514	531	547	564	581	597	614	631	647
61	664	681	697	714	731	747	764	780	797	814
62	830	817	863	880	896	913	929	946	963	979
63	996	*012	*029	*045	*062	*078	*095	*111	*127	*144
64	42 160	177	193	210	226	243	259	275	292	308
65	325	341	357	374	390	406	423	439	455	472
66	488	504	521	537	553	570	586	602	619	635
67	651	667	684	700	716	732	749	765	781	797
68	813	830	846	862	878	894	911	927	943	959
69	975	991	*008	*024	*040	*056	*072	*088	*104	*120
270	43 136	152	169	185	201	217	233	249	265	281
71	297	313	329	345	361	377	393	409	425	441
72	457	473	489	505	521	537	553	569	584	600
73	616	632	648	664	680	696	712	727	743	759
74	775	791	807	823	838	854	870	886	902	917
75	933	949	965	981	996	*012	*028	*044	*059	*075
76	44 091	107	122	138	154	170	185	201	217	232
77	248	264	279	295	311	326	342	358	373	389
78	404	420	436	451	467	483	498	514	529	545
79	560	576	592	607	623	638	654	669	685	700
280	716	731	747	762	778	793	809	824	840	855
81	871	886	902	917	932	948	963	979	994	*010
82	45 025	040	056	071	086	102	117	133	148	163
83	179	194	209	225	240	255	271	286	301	317
84	332	347	362	378	393	408	423	439	454	469
85	484	500	515	530	545	561	576	591	606	621
86	637	652	667	682	697	712	728	743	758	773
87	788	803	818	834	849	864	879	894	909	924
88	939	954	969	984	*000	*015	*030	*045	*060	*075
89	46 090	105	120	135	150	165	180	195	210	225
290	240	255	270	285	300	315	330	345	359	374
91	389	404	419	434	449	464	479	494	509	523
92	538	553	568	583	598	613	627	642	657	672
93	687	702	716	731	746	761	776	790	805	820
94	835	850	864	879	894	909	923	938	953	967
95	982	997	*012	*026	*041	*056	*070	*085	*100	*114
96	47 129	144	159	173	188	202	217	232	246	261
97	276	290	305	319	334	349	363	378	392	407
98	422	436	451	465	480	494	509	524	538	553
99	567	582	596	611	625	640	654	669	683	698
300	712	727	741	756	770	784	799	813	828	842
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

PP

	18
1	1.8
2	3.6
3	5.4
4	7.2
5	9.0
6	10.8
7	12.6
8	14.4
9	16.2

	17
1	1.7
2	3.4
3	5.1
4	6.8
5	8.5
6	10.2
7	11.9
8	13.6
9	15.3

	16
1	1.6
2	3.2
3	4.8
4	6.4
5	8.0
6	9.6
7	11.2
8	12.8
9	14.4

	15
1	1.5
2	3.0
3	4.5
4	6.0
5	7.5
6	9.0
7	10.5
8	12.0
9	13.5

	14
1	1.4
2	2.8
3	4.2
4	5.6
5	7.0
6	8.4
7	9.8
8	11.2
9	12.6

PP

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
300	47 712	727	741	756	770	784	799	813	828	842
01	857	871	885	900	914	929	943	958	972	986
02	48 001	015	029	044	058	073	087	101	116	130
03	144	159	173	187	202	216	230	244	259	273
04	287	302	316	330	344	359	373	387	401	416
05	430	444	458	473	487	501	515	530	544	558
06	572	586	601	615	629	643	657	671	686	700
07	714	728	742	756	770	785	799	813	827	841
08	855	869	883	897	911	926	940	954	968	982
09	996	*010	*024	*038	*052	*066	*080	*094	*108	*122
310	49 136	150	164	178	192	206	220	234	248	262
11	276	290	304	318	332	346	360	374	388	402
12	415	429	443	457	471	485	499	513	527	541
13	554	568	582	596	610	624	638	651	665	679
14	693	707	721	734	748	762	776	790	803	817
15	831	845	859	872	886	900	914	927	941	955
16	969	982	996	*010	*024	*037	*051	*065	*079	*092
17	50 106	120	133	147	161	174	188	202	215	229
18	243	256	270	284	297	311	325	338	352	365
19	379	393	406	420	433	447	461	474	488	501
320	515	529	542	556	569	583	596	610	623	637
21	651	664	678	691	705	718	732	745	759	772
22	786	799	813	826	840	853	866	880	893	907
23	920	934	947	961	974	987	*001	*014	*028	*041
24	51 055	068	081	095	108	121	135	148	162	175
25	188	202	215	228	242	255	268	282	295	308
26	322	335	348	362	375	388	402	415	428	441
27	455	468	481	495	508	521	534	548	561	574
28	587	601	614	627	640	654	667	680	693	706
29	720	733	746	759	772	786	799	812	825	838
330	851	865	878	891	904	917	930	943	957	970
31	983	996	*009	*022	*035	*048	*061	*075	*088	*101
32	52 114	127	140	153	166	179	192	205	218	231
33	244	257	270	284	297	310	323	336	349	362
34	375	388	401	414	427	440	453	466	479	492
35	504	517	530	543	556	569	582	595	608	621
36	634	647	660	673	686	699	711	724	737	750
37	763	776	789	802	815	827	840	853	866	879
38	892	905	917	930	943	956	969	982	994	*007
39	53 020	033	046	058	071	084	097	110	122	135
340	148	161	173	186	199	212	224	237	250	263
41	275	288	301	314	326	339	352	364	377	390
42	403	415	428	441	453	466	479	491	504	517
43	529	542	555	567	580	593	605	618	631	643
44	656	668	681	694	706	719	732	744	757	769
45	782	794	807	820	832	845	857	870	882	895
46	908	920	933	945	958	970	983	995	*008	*020
47	54 033	045	058	070	083	095	108	120	133	145
48	158	170	183	195	208	220	233	245	258	270
49	283	295	307	320	332	345	357	370	382	394
350	407	419	432	444	456	469	481	494	506	518
N	0	1	2	3	4	5	6	7	8	9

P P

	15
1	1.5
2	3.0
3	4.5
4	6.0
5	7.5
6	9.0
7	10.5
8	12.0
9	13.5

	14
1	1.4
2	2.8
3	4.2
4	5.6
5	7.0
6	8.4
7	9.8
8	11.2
9	12.6

	13
1	1.3
2	2.6
3	3.9
4	5.2
5	6.5
6	7.8
7	9.1
8	10.4
9	11.7

	12
1	1.2
2	2.4
3	3.6
4	4.8
5	6.0
6	7.2
7	8.4
8	9.6
9	10.8

P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
350	54 407	419	432	444	456	469	481	494	506	518
51	531	543	555	568	580	593	605	617	630	642
52	654	667	679	691	704	716	728	741	753	765
53	777	790	802	814	827	839	851	864	876	888
54	900	913	925	937	949	962	974	986	998	*011
55	55 023	035	047	060	072	084	096	108	121	133
56	145	157	169	182	194	206	218	230	242	255
57	267	279	291	303	315	328	340	352	364	376
58	388	400	413	425	437	449	461	473	485	497
59	509	522	534	546	558	570	582	594	606	618
360	630	642	654	666	678	691	703	715	727	739
61	751	763	775	787	799	811	823	835	847	859
62	871	883	895	907	919	931	943	955	967	979
63	991	*003	*015	*027	*038	*050	*062	*074	*086	*098
64	56 110	122	134	146	158	170	182	194	205	217
65	229	241	253	265	277	289	301	312	324	336
66	348	360	372	384	396	407	419	431	443	455
67	467	478	490	502	514	526	538	549	561	573
68	585	597	608	620	632	644	656	667	679	691
69	703	714	726	738	750	761	773	785	797	803
370	820	832	844	855	867	879	891	902	914	926
71	937	949	961	972	984	996	*008	*019	*031	*043
72	57 054	066	078	089	101	113	124	136	148	159
73	171	183	194	206	217	229	241	252	264	276
74	287	299	310	322	334	345	357	368	380	392
75	403	415	426	438	449	461	473	484	496	507
76	519	530	542	553	565	576	588	600	611	623
77	634	646	657	669	680	692	703	715	726	738
78	749	761	772	784	795	807	818	830	841	852
79	864	875	887	898	910	921	933	944	955	967
380	978	990	*001	*013	*024	*035	*047	*058	*070	*081
81	58 092	104	115	127	138	149	161	172	184	195
82	206	218	229	240	252	263	274	286	297	309
83	320	331	343	354	365	377	388	399	410	422
84	433	444	456	467	478	490	501	512	524	535
85	546	557	569	580	591	602	614	625	636	647
86	659	670	681	692	704	715	726	737	749	760
87	771	782	794	805	816	827	838	850	861	872
88	883	894	906	917	928	939	950	961	973	984
89	995	*006	*017	*028	*040	*051	*062	*073	*084	*095
390	59 106	118	129	140	151	162	173	184	195	207
91	218	229	240	251	262	273	284	295	306	318
92	329	340	351	362	373	384	395	406	417	428
93	439	450	461	472	483	494	506	517	528	539
94	550	561	572	583	594	605	616	627	638	649
95	660	671	682	693	704	715	726	737	748	759
96	770	780	791	802	813	824	835	846	857	868
97	879	890	901	912	923	934	945	956	966	977
98	988	999	*010	*021	*032	*043	*054	*065	*076	*086
99	60 097	108	119	130	141	152	163	173	184	195
400	206	217	228	239	249	260	271	282	293	304
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

P P

	13
1	1.3
2	2.6
3	3.9
4	5.2
5	6.5
6	7.8
7	9.1
8	10.4
9	11.7

	12
1	1.2
2	2.4
3	3.6
4	4.8
5	6.0
6	7.2
7	8.4
8	9.6
9	10.8

	11
1	1.1
2	2.2
3	3.3
4	4.4
5	5.5
6	6.6
7	7.7
8	8.8
9	9.9

	10
1	1.0
2	2.0
3	3.0
4	4.0
5	5.0
6	6.0
7	7.0
8	8.0
9	9.0

P P

Table I.—Common Logarithms of Numbers

To Five Decimal Places

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	
01	314	325	336	347	358	369	379	390	401	412	
02	423	433	444	455	466	477	487	498	509	520	
03	531	541	552	563	574	584	595	606	617	627	
04	638	649	660	670	681	692	703	713	724	735	
05	746	756	767	778	788	799	810	821	831	842	
06	853	863	874	885	895	906	917	927	938	949	
07	959	970	981	991	*002	*013	*023	*034	*045	*055	
08	61 066	077	087	098	109	119	130	140	151	162	
09	172	183	194	204	215	225	236	247	257	268	
410	278	289	300	310	321	331	342	352	363	374	
11	384	395	405	416	426	437	448	458	469	479	
12	490	500	511	521	532	542	553	563	574	584	
13	595	606	616	627	637	648	658	669	679	690	
14	700	711	721	731	742	752	763	773	784	794	
15	805	815	826	836	847	857	868	878	888	899	
16	909	920	930	941	951	962	972	982	993	*003	
17	62 014	024	034	045	055	066	076	086	097	107	
18	118	128	138	149	159	170	180	190	201	211	
19	221	232	242	252	263	273	284	294	304	315	
420	325	335	346	356	366	377	387	397	408	418	
21	428	439	449	459	469	480	490	500	511	521	
22	531	542	552	562	572	583	593	603	613	624	
23	634	644	655	665	675	685	696	706	716	726	
24	737	747	757	767	778	788	798	808	818	829	
25	839	849	859	870	880	890	900	910	921	931	
26	941	951	961	972	982	992	*002	*012	*022	*033	
27	63 043	053	063	073	083	094	104	114	124	134	
28	144	155	165	175	185	195	205	215	225	236	
29	246	256	266	276	286	296	306	317	327	337	
430	347	357	367	377	387	397	407	417	428	438	
31	448	458	468	478	488	498	508	518	528	538	
32	548	558	568	579	589	599	609	619	629	639	
33	649	659	669	679	689	699	709	719	729	739	
34	749	759	769	779	789	799	809	819	829	839	
35	849	859	869	879	889	899	909	919	929	939	
36	949	959	969	979	988	998	*008	*018	*028	*038	
37	64 048	058	068	078	088	098	108	118	128	137	
38	147	157	167	177	187	197	207	217	227	237	
39	246	256	266	276	286	296	306	316	326	335	
440	345	355	365	375	385	395	404	414	424	434	
41	444	454	464	473	483	493	503	513	523	532	
42	542	552	562	572	582	591	601	611	621	631	
43	640	650	660	670	680	689	699	709	719	729	
44	738	748	758	768	777	787	797	807	816	826	
45	836	846	856	865	875	885	895	904	914	924	
46	933	943	953	963	972	982	992	*002	*011	*021	
47	65 031	040	050	060	070	079	089	099	108	118	
48	128	137	147	157	167	176	186	196	205	215	
49	225	234	244	254	263	273	283	292	302	312	
450	321	331	341	350	360	369	379	389	398	408	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**P P**

	11
1	1.1
2	2.2
3	3.3
4	4.4
5	5.5
6	6.6
7	7.7
8	8.8
9	9.9

	10
1	1.0
2	2.0
3	3.0
4	4.0
5	5.0
6	6.0
7	7.0
8	8.0
9	9.0

	9
1	0.9
2	1.8
3	2.7
4	3.6
5	4.5
6	5.4
7	6.3
8	7.2
9	8.1

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
450	65 321	331	341	350	360	369	379	389	398	408
51	418	427	437	447	456	466	475	485	495	504
52	514	523	533	543	552	562	571	581	591	600
53	610	619	629	639	648	658	667	677	686	696
54	706	715	725	734	744	753	763	772	782	792
55	801	811	820	830	839	849	858	868	877	887
56	896	906	916	925	935	944	954	963	973	982
57	992	*001	*011	*020	*030	*039	*049	*058	*068	*077
58	66 087	096	106	115	124	134	143	153	162	172
59	181	191	200	210	219	229	238	247	257	266
460	276	285	295	304	314	323	332	342	351	361
61	370	380	389	398	408	417	427	436	445	455
62	464	474	483	492	502	511	521	530	539	549
63	558	567	577	586	596	605	614	624	633	642
64	652	661	671	680	689	699	708	717	727	736
65	745	755	764	773	783	792	801	811	820	829
66	839	848	857	867	876	885	894	904	913	922
67	932	941	950	960	969	978	987	997	*006	*015
68	67 025	034	043	052	062	071	080	089	099	108
69	117	127	136	145	154	164	173	182	191	201
470	210	219	228	237	247	256	265	274	284	293
71	302	311	321	330	339	348	357	367	376	385
72	394	403	413	422	431	440	449	459	468	477
73	486	495	504	514	523	532	541	550	560	569
74	578	587	596	605	614	624	633	642	651	660
75	669	679	688	697	706	715	724	733	742	752
76	761	770	779	788	797	806	815	825	834	843
77	852	861	870	879	888	897	906	916	925	934
78	943	952	961	970	979	988	997	*006	*015	*024
79	68 034	043	052	061	070	079	088	097	106	115
480	124	133	142	151	160	169	178	187	196	205
81	215	224	233	242	251	260	269	278	287	296
82	305	314	323	332	341	350	359	368	377	386
83	395	404	413	422	431	440	449	458	467	476
84	485	494	502	511	520	529	538	547	556	565
85	574	583	592	601	610	619	628	637	646	655
86	664	673	681	690	699	708	717	726	735	744
87	753	762	771	780	789	797	806	815	824	833
88	842	851	860	869	878	886	895	904	913	922
89	931	940	949	958	966	975	984	993	*002	*011
490	69 020	028	037	046	055	064	073	082	090	099
91	108	117	126	135	144	152	161	170	179	188
92	197	205	214	223	232	241	249	258	267	276
93	285	294	302	311	320	329	338	346	355	364
94	373	381	390	399	408	417	425	434	443	452
95	461	469	478	487	496	504	513	522	531	539
96	548	557	566	574	583	592	601	609	618	627
97	636	644	653	662	671	679	688	697	705	714
98	723	732	740	749	758	767	775	784	793	801
99	810	819	827	836	845	854	862	871	880	888
500	897	906	914	923	932	940	949	958	966	975
N	0	1	2	3	4	5	6	7	8	9

P P

	10
1	1.0
2	2.0
3	3.0
4	4.0
5	5.0
6	6.0
7	7.0
8	8.0
9	9.0

	9
1	0.9
2	1.8
3	2.7
4	3.6
5	4.5
6	5.4
7	6.3
8	7.2
9	8.1

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9	P P
500	69 897	906	914	923	932	940	949	958	966	975	
01	984	992	*001	*010	*018	*027	*036	*044	*053	*062	
02	70 070	079	088	096	105	114	122	131	140	148	
03	157	165	174	183	191	200	209	217	226	234	
04	243	252	260	269	278	286	295	303	312	321	
05	329	338	346	355	364	372	381	389	398	406	
06	415	424	432	441	449	458	467	475	484	492	
07	501	509	518	526	535	544	552	561	569	578	
08	586	595	603	612	621	629	638	646	655	663	9 1 0.9 2 1.8 3 2.7 4 3.6 5 4.5 6 5.4 7 6.3 8 7.2 9 8.1
09	672	680	689	697	706	714	723	731	740	749	
510	757	766	774	783	791	800	808	817	825	834	
11	842	851	859	868	876	885	893	902	910	919	
12	927	935	944	952	961	969	978	986	995	*003	
13	71 012	020	029	037	046	054	063	071	079	088	
14	096	105	113	122	130	139	147	155	164	172	
15	181	189	198	206	214	223	231	240	248	257	
16	265	273	282	290	299	307	315	324	332	341	
17	349	357	366	374	383	391	399	408	416	425	
18	433	441	450	458	466	475	483	492	500	508	
19	517	525	533	542	550	559	567	575	584	592	
520	600	609	617	625	634	642	650	659	667	675	
21	684	692	700	709	717	725	734	742	750	759	
22	767	775	784	792	800	809	817	825	834	842	
23	850	858	867	875	883	892	900	908	917	925	8 1 0.8 2 1.6 3 2.4 4 3.2 5 4.0 6 4.8 7 5.6 8 6.4 9 7.2
24	933	941	950	958	966	975	983	991	999	*008	
25	72 016	024	032	041	049	057	066	074	082	090	
26	099	107	115	123	132	140	148	156	165	173	
27	181	189	198	206	214	222	230	239	247	255	
28	263	272	280	288	296	304	313	321	329	337	
29	346	354	362	370	378	387	395	403	411	419	
530	428	436	444	452	460	469	477	485	493	501	
31	509	518	526	534	542	550	558	567	575	583	
32	591	599	607	616	624	632	640	648	656	665	
33	673	681	689	697	705	713	722	730	738	746	
34	754	762	770	779	787	795	803	811	819	827	
35	835	843	852	860	868	876	884	892	900	908	
36	916	925	933	941	949	957	965	973	981	989	
37	997	*006	*014	*022	*030	*038	*046	*054	*062	*070	7 1 0.7 2 1.4 3 2.1 4 2.8 5 3.5 6 4.2 7 4.9 8 5.6 9 6.3
38	73 078	086	094	102	111	119	127	135	143	151	
39	159	167	175	183	191	199	207	215	223	231	
540	239	247	255	263	272	280	288	296	304	312	
41	320	328	336	344	352	360	368	376	384	392	
42	400	408	416	424	432	440	448	456	464	472	
43	480	488	496	504	512	520	528	536	544	552	
44	560	568	576	584	592	600	608	616	624	632	
45	640	648	656	664	672	679	687	695	703	711	
46	719	727	735	743	751	759	767	775	783	791	
47	799	807	815	823	830	838	846	854	862	870	
48	878	886	894	902	910	918	926	933	941	949	
49	957	965	973	981	989	997	*005	*013	*020	*028	
550	74 036	044	052	060	068	076	084	092	099	107	
N	0	1	2	3	4	5	6	7	8	9	P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

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	
51	115	123	131	139	147	155	162	170	178	186	
52	194	202	210	218	225	233	241	249	257	265	
53	273	280	288	296	304	312	320	327	335	343	
54	351	359	367	374	382	390	398	406	414	421	
55	429	437	445	453	461	468	476	484	492	500	
56	507	515	523	531	539	547	554	562	570	578	
57	586	593	601	609	617	624	632	640	648	656	
58	663	671	679	687	695	702	710	718	726	733	
59	741	749	757	764	772	780	788	796	803	811	
560	819	827	834	842	850	858	865	873	881	889	
61	896	904	912	920	927	935	943	950	958	966	
62	974	981	989	997	*005	*012	*020	*028	*035	*043	
63	75 051	059	066	074	082	089	097	105	113	120	
64	128	136	143	151	159	166	174	182	189	197	
65	205	213	220	228	236	243	251	259	266	274	
66	282	289	297	305	312	320	328	335	343	351	
67	358	366	374	381	389	397	404	412	420	427	
68	435	442	450	458	465	473	481	488	496	504	
69	511	519	526	534	542	549	557	565	572	580	
570	587	595	603	610	618	626	633	641	648	656	
71	664	671	679	686	694	702	709	717	724	732	
72	740	747	755	762	770	778	785	793	800	808	
73	815	823	831	838	846	853	861	868	876	884	
74	891	899	906	914	921	929	937	944	952	959	
75	967	974	982	989	997	*005	*012	*020	*027	*035	
76	76 042	050	057	065	072	080	087	095	103	110	
77	118	125	133	140	148	155	163	170	178	185	
78	193	200	208	215	223	230	238	245	253	260	
79	268	275	283	290	298	305	313	320	328	335	
580	343	350	358	365	373	380	388	395	403	410	
81	418	425	433	440	448	455	462	470	477	485	
82	492	500	507	515	522	530	537	545	552	559	
83	567	574	582	589	597	604	612	619	626	634	
84	641	649	656	664	671	678	686	693	701	708	
85	716	723	730	738	745	753	760	768	775	782	
86	790	797	805	812	819	827	834	842	849	856	
87	864	871	879	886	893	901	908	916	923	930	
88	938	945	953	960	967	975	982	989	997	*004	
89	77 012	019	026	034	041	048	056	063	070	078	
590	085	093	100	107	115	122	129	137	144	151	
91	159	166	173	181	188	195	203	210	217	225	
92	232	240	247	254	262	269	276	283	291	298	
93	305	313	320	327	335	342	349	357	364	371	
94	379	386	393	401	408	415	422	430	437	444	
95	452	459	466	474	481	488	495	503	510	517	
96	525	532	539	546	554	561	568	576	583	590	
97	597	605	612	619	627	634	641	648	656	663	
98	670	677	685	692	699	706	714	721	728	735	
99	743	750	757	764	772	779	786	793	801	808	
600	815	822	830	837	844	851	859	866	873	880	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**P P**

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

TABLE I.—COMMON LOGARITHMS OF NUMBERS
To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
600	77 815	822	830	837	844	851	859	866	873	880
01	887	895	902	909	916	924	931	938	945	952
02	960	967	974	981	988	996	*003	*010	*017	*025
03	78 032	039	046	053	061	068	075	082	089	097
04	104	111	118	125	132	140	147	154	161	168
05	176	183	190	197	204	211	219	226	233	240
06	247	254	262	269	276	283	290	297	305	312
07	319	326	333	340	347	355	362	369	376	383
08	390	398	405	412	419	426	433	440	447	455
09	462	469	476	483	490	497	504	512	519	526
610	533	540	547	554	561	569	576	583	590	597
11	604	611	618	625	633	640	647	654	661	668
12	675	682	689	696	704	711	718	725	732	739
13	746	753	760	767	774	781	789	796	803	810
14	817	824	831	838	845	852	859	866	873	880
15	888	895	902	909	916	923	930	937	944	951
16	958	965	972	979	986	993	*000	*007	*014	*021
17	79 029	036	043	050	057	064	071	078	085	092
18	099	106	113	120	127	134	141	148	155	162
19	169	176	183	190	197	204	211	218	225	232
620	239	246	253	260	267	274	281	288	295	302
21	309	316	323	330	337	344	351	358	365	372
22	379	386	393	400	407	414	421	428	435	442
23	449	456	463	470	477	484	491	498	505	511
24	518	525	532	539	546	553	560	567	574	581
25	588	595	602	609	616	623	630	637	644	650
26	657	664	671	678	685	692	699	706	713	720
27	727	734	741	748	754	761	768	775	782	789
28	796	803	810	817	824	831	837	844	851	858
29	865	872	879	886	893	900	906	913	920	927
630	934	941	948	955	962	969	975	982	989	996
31	80 003	010	017	024	030	037	044	051	058	065
32	072	079	085	092	099	106	113	120	127	134
33	140	147	154	161	168	175	182	188	195	202
34	209	216	223	229	236	243	250	257	264	271
35	277	284	291	298	305	312	318	325	332	339
36	346	353	359	366	373	380	387	393	400	407
37	414	421	428	434	441	448	455	462	468	475
38	482	489	496	502	509	516	523	530	536	543
39	550	557	564	570	577	584	591	598	604	611
640	618	625	632	638	645	652	659	665	672	679
41	686	693	699	706	713	720	726	733	740	747
42	754	760	767	774	781	787	794	801	808	814
43	821	828	835	841	848	855	862	868	875	882
44	889	895	902	909	916	922	929	936	943	949
45	956	963	969	976	983	990	996	*003	*010	*017
46	81 023	030	037	043	050	057	064	070	077	084
47	090	097	104	111	117	124	131	137	144	151
48	158	164	171	178	184	191	198	204	211	218
49	224	231	238	245	251	258	265	271	278	285
650	291	298	305	311	318	325	331	338	345	351
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**

P P

	8
1	0.8
2	1.6
3	2.4
4	3.2
5	4.0
6	4.8
7	5.6
8	6.4
9	7.2

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
650	81 291	298	305	311	318	325	331	338	345	351
51	358	365	371	378	385	391	398	405	411	418
52	425	431	438	445	451	458	465	471	478	485
53	491	498	505	511	518	525	531	538	544	551
54	558	564	571	578	584	591	598	604	611	617
55	624	631	637	644	651	657	664	671	677	684
56	690	697	704	710	717	723	730	737	743	750
57	757	763	770	776	783	790	796	803	809	816
58	823	829	836	842	849	856	862	869	875	882
59	889	895	902	908	915	921	928	935	941	948
660	954	961	968	974	981	987	994	*000	*007	*014
61	82 020	027	033	040	046	053	060	066	073	079
62	086	092	099	105	112	119	125	132	138	145
63	151	158	164	171	178	184	191	197	204	210
64	217	223	230	236	243	249	256	263	269	276
65	282	289	295	302	308	315	321	328	334	341
66	347	354	360	367	373	380	387	393	400	406
67	413	419	426	432	439	445	452	458	465	471
68	478	484	491	497	504	510	517	523	530	536
69	543	549	556	562	569	575	582	588	595	601
670	607	614	620	627	633	640	646	653	659	666
71	672	679	685	692	698	705	711	718	724	730
72	737	743	750	756	763	769	776	782	789	795
73	802	808	814	821	827	834	840	847	853	860
74	866	872	879	885	892	898	905	911	918	924
75	930	937	943	950	956	963	969	975	982	988
76	995	*001	*008	*014	*020	*027	*033	*040	*046	*052
77	83 059	065	072	078	085	091	097	104	110	117
78	123	129	136	142	149	155	161	168	174	181
79	187	193	200	206	213	219	225	232	238	245
680	251	257	264	270	276	283	289	296	302	308
81	315	321	327	334	340	347	353	359	366	372
82	378	385	391	398	404	410	417	423	429	436
83	442	448	455	461	467	474	480	487	493	499
84	506	512	518	525	531	537	544	550	556	563
85	569	575	582	588	594	601	607	613	620	626
86	632	639	645	651	658	664	670	677	683	689
87	696	702	708	715	721	727	734	740	746	753
88	759	765	771	778	784	790	797	803	809	816
89	822	828	835	841	847	853	860	866	872	879
690	885	891	897	904	910	916	923	929	935	942
91	948	954	960	967	973	979	985	992	998	*004
92	84 011	017	023	029	036	042	048	055	061	067
93	073	080	086	092	098	105	111	117	123	130
94	136	142	148	155	161	167	173	180	186	192
95	198	205	211	217	223	230	236	242	248	255
96	261	267	273	280	286	292	298	305	311	317
97	323	330	336	342	348	354	361	367	373	379
98	386	392	398	404	410	417	423	429	435	442
99	448	454	460	466	473	479	485	491	497	504
700	510	516	522	528	535	541	547	553	559	566
N	0	1	2	3	4	5	6	7	8	9

P P

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
700	84 510	516	522	528	535	541	547	553	559	566
01	572	578	584	590	597	603	609	615	621	628
02	634	640	646	652	658	665	671	677	683	689
03	696	702	708	714	720	726	733	739	745	751
04	757	763	770	776	782	788	794	800	807	813
05	819	825	831	837	844	850	856	862	868	874
06	880	887	893	899	905	911	917	924	930	936
07	942	948	954	960	967	973	979	985	991	997
08	85 003	009	016	022	028	034	040	046	052	058
09	065	071	077	083	089	095	101	107	114	120
710	126	132	138	144	150	156	163	169	175	181
11	187	193	199	205	211	217	224	230	236	242
12	248	254	260	266	272	278	285	291	297	303
13	309	315	321	327	333	339	345	352	358	364
14	370	376	382	388	394	400	406	412	418	425
15	431	437	443	449	455	461	467	473	479	485
16	491	497	503	509	516	522	528	534	540	546
17	552	558	564	570	576	582	588	594	600	606
18	612	618	625	631	637	643	649	655	661	667
19	673	679	685	691	697	703	709	715	721	727
720	733	739	745	751	757	763	769	775	781	788
21	794	800	806	812	818	824	830	836	842	848
22	854	860	866	872	878	884	890	896	902	908
23	914	920	926	932	938	944	950	956	962	968
24	974	980	986	992	998	*004	*010	*016	*022	*028
25	86 034	040	046	052	058	064	070	076	082	088
26	094	100	106	112	118	124	130	136	141	147
27	153	159	165	171	177	183	189	195	201	207
28	213	219	225	231	237	243	249	255	261	267
29	273	279	285	291	297	303	308	314	320	326
730	332	338	344	350	356	362	368	374	380	386
31	392	398	404	410	415	421	427	433	439	445
32	451	457	463	469	475	481	487	493	499	504
33	510	516	522	528	534	540	546	552	558	564
34	570	576	581	587	593	599	605	611	617	623
35	629	635	641	646	652	658	664	670	676	682
36	688	694	700	705	711	717	723	729	735	741
37	747	753	759	764	770	776	782	788	794	800
38	806	812	817	823	829	835	841	847	853	859
39	864	870	876	882	888	894	900	906	911	917
740	923	929	935	941	947	953	958	964	970	976
41	982	988	994	999	*005	*011	*017	*023	*029	*035
42	87 040	046	052	058	064	070	075	081	087	093
43	099	105	111	116	122	128	134	140	146	151
44	157	163	169	175	181	186	192	198	204	210
45	216	221	227	233	239	245	251	256	262	268
46	274	280	286	291	297	303	309	315	320	326
47	332	338	344	349	355	361	367	373	379	384
48	390	396	402	408	413	419	425	431	437	442
49	448	454	460	466	471	477	483	489	495	500
750	506	512	518	523	529	535	541	547	552	558
N	0	1	2	3	4	5	6	7	8	9

P P

	7
1	0.7
2	1.4
3	2.1
4	2.8
5	3.5
6	4.2
7	4.9
8	5.6
9	6.3

	6
1	0.6
2	1.2
3	1.8
4	2.4
5	3.0
6	3.6
7	4.2
8	4.8
9	5.4

	5
1	0.5
2	1.0
3	1.5
4	2.0
5	2.5
6	3.0
7	3.5
8	4.0
9	4.5

P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS
To Five Decimal Places

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	
51	564	570	576	581	587	593	599	604	610	616	
52	622	628	633	639	645	651	656	662	668	574	
53	679	685	691	697	703	708	714	720	726	731	
54	737	743	749	754	760	766	772	777	783	789	
55	795	800	806	812	818	823	829	835	841	846	
56	852	858	864	869	875	881	887	892	898	904	
57	910	915	921	927	933	938	944	950	955	961	
58	967	973	978	984	990	996	*001	*007	*013	*018	
59	88 024	030	036	041	047	053	058	064	070	076	
760	081	087	093	098	104	110	116	121	127	133	
61	138	144	150	156	161	167	173	178	184	190	
62	195	201	207	213	218	224	230	235	241	247	
63	252	258	264	270	275	281	287	292	298	304	
64	309	315	321	326	332	338	343	349	355	360	
65	366	372	377	383	389	395	400	406	412	417	
66	423	429	434	440	446	451	457	463	468	474	
67	480	485	491	497	502	508	513	519	525	530	
68	536	542	547	553	559	564	570	576	581	587	
69	593	598	604	610	615	621	627	632	638	643	
770	649	655	660	666	672	677	683	689	694	700	
71	705	711	717	722	728	734	739	745	750	756	
72	762	767	773	779	784	790	795	801	807	812	
73	818	824	829	835	840	846	852	857	863	868	
74	874	880	885	891	897	902	908	913	919	925	
75	930	936	941	947	953	958	964	969	975	981	
76	986	992	997	*003	*009	*014	*020	*025	*031	*037	
77	89 042	048	053	059	064	070	076	081	087	092	
78	098	104	109	115	120	126	131	137	143	148	
79	154	159	165	170	176	182	187	193	198	204	
780	209	215	221	226	232	237	243	248	254	260	
81	265	271	276	282	287	293	298	304	310	315	
82	321	326	332	337	343	348	354	360	365	371	
83	376	382	387	393	398	404	409	415	421	426	
84	432	437	443	448	454	459	465	470	476	481	
85	487	492	498	504	509	515	520	526	531	537	
86	542	548	553	559	564	570	575	581	586	592	
87	597	603	609	614	620	625	631	636	642	647	
88	653	658	664	669	675	680	686	691	697	702	
89	708	713	719	724	730	735	741	746	752	757	
790	763	768	774	779	785	790	796	801	807	812	
91	818	823	829	834	840	845	851	856	862	867	
92	873	878	883	889	894	900	905	911	916	922	
93	927	933	938	944	949	955	960	966	971	977	
94	982	988	993	998	*004	*009	*015	*020	*026	*031	
95	90 037	042	048	053	059	064	069	075	080	086	
96	091	097	102	108	113	119	124	129	135	140	
97	146	151	157	162	168	173	179	184	189	195	
98	200	206	211	217	222	227	233	238	244	249	
99	255	260	266	271	276	282	287	293	298	304	
800	309	314	320	325	331	336	342	347	352	358	
N	0	1	2	3	4	5	6	7	8	9	P P

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2	1.2
3	1.8
4	2.4
5	3.0
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7	4.2
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9	5.4

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8	4.0
9	4.5

TABLE I.—COMMON LOGARITHMS OF NUMBERS
To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9
800	90 309	314	320	325	331	336	342	347	352	358
01	363	369	374	380	385	390	396	401	407	412
02	417	423	428	434	439	445	450	455	461	466
03	472	477	482	488	493	499	504	509	515	520
04	526	531	536	542	547	553	558	563	569	574
05	580	585	590	596	601	607	612	617	623	628
06	634	639	644	650	655	660	666	671	677	682
07	687	693	698	703	709	714	720	725	730	736
08	741	747	752	757	763	768	773	779	784	789
09	795	800	806	811	816	822	827	832	838	843
810	849	854	859	865	870	875	881	886	891	897
11	902	907	913	918	924	929	934	940	945	950
12	956	961	966	972	977	982	988	993	998	*004
13	91 009	014	020	025	030	036	041	046	052	057
14	062	068	073	078	084	089	094	100	105	110
15	116	121	126	132	137	142	148	153	158	164
16	169	174	180	185	190	196	201	206	212	217
17	222	228	233	238	243	249	254	259	265	270
18	275	281	286	291	297	302	307	312	318	323
19	328	334	339	344	350	355	360	365	371	376
820	381	387	392	397	403	408	413	418	424	429
21	434	440	445	450	455	461	466	471	477	482
22	487	492	498	503	508	514	519	524	529	535
23	540	545	551	556	561	566	572	577	582	587
24	593	598	603	609	614	619	624	630	635	640
25	645	651	656	661	666	672	677	682	687	693
26	698	703	709	714	719	724	730	735	740	745
27	751	756	761	766	772	777	782	787	793	798
28	803	808	814	819	824	829	834	840	845	850
29	855	861	866	871	876	882	887	892	897	903
830	908	913	918	924	929	934	939	944	950	955
31	960	965	971	976	981	986	991	997	*002	*007
32	92 012	018	023	028	033	038	044	049	054	059
33	065	070	075	080	085	091	096	101	106	111
34	117	122	127	132	137	143	148	153	158	163
35	169	174	179	184	189	195	200	205	210	215
36	221	226	231	236	241	247	252	257	262	267
37	273	278	283	288	293	298	304	309	314	319
38	324	330	335	340	345	350	355	361	366	371
39	376	381	387	392	397	402	407	412	418	423
840	428	433	438	443	449	454	459	464	469	474
41	480	485	490	495	500	505	511	516	521	526
42	531	536	542	547	552	557	562	567	572	578
43	583	588	593	598	603	609	614	619	624	629
44	634	639	645	650	655	660	665	670	675	681
45	686	691	696	701	706	711	716	722	727	732
46	737	742	747	752	758	763	768	773	778	783
47	788	793	799	804	809	814	819	824	829	834
48	840	845	850	855	860	865	870	875	881	886
49	891	896	901	906	911	916	921	927	932	937
850	942	947	952	957	962	967	973	978	983	988
N	0	1	2	3	4	5	6	7	8	9

P P

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3	1.8
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8	4.8
9	5.4

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3	1.5
4	2.0
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7	3.5
8	4.0
9	4.5

P P

TABLE I.—COMMON LOGARITHMS OF NUMBERS
To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9	P P
850	92 942	947	952	957	962	967	973	978	983	988	
51	993	998	*003	*008	*013	*018	*024	*029	*034	*039	
52	93 044	049	054	059	064	069	075	080	085	090	
53	095	100	105	110	115	120	125	131	136	141	
54	146	151	156	161	166	171	176	181	186	192	
55	197	202	207	212	217	222	227	232	237	242	
56	247	252	258	263	268	273	278	283	288	293	
57	298	303	308	313	318	323	328	334	339	344	
58	349	354	359	364	369	374	379	384	389	394	
59	399	404	409	414	420	425	430	435	440	445	
860	450	455	460	465	470	475	480	485	490	495	
61	500	505	510	515	520	526	531	536	541	546	
62	551	556	561	566	571	576	581	586	591	596	
63	601	606	611	616	621	626	631	636	641	646	
64	651	656	661	666	671	676	682	687	692	697	
65	702	707	712	717	722	727	732	737	742	747	
66	752	757	762	767	772	777	782	787	792	797	
67	802	807	812	817	822	827	832	837	842	847	
68	852	857	862	867	872	877	882	887	892	897	
69	902	907	912	917	922	927	932	937	942	947	
870	952	957	962	967	972	977	982	987	992	997	
71	94 002	007	012	017	022	027	032	037	042	047	
72	052	057	062	067	072	077	082	086	091	096	
73	101	106	111	116	121	126	131	136	141	146	
74	151	156	161	166	171	176	181	186	191	196	
75	201	206	211	216	221	226	231	236	240	245	
76	250	255	260	265	270	275	280	285	290	295	
77	300	305	310	315	320	325	330	335	340	345	
78	349	354	359	364	369	374	379	384	389	394	
79	399	404	409	414	419	424	429	433	438	443	
880	448	453	458	463	468	473	478	483	488	493	
81	498	503	507	512	517	522	527	532	537	542	
82	547	552	557	562	567	571	576	581	586	591	
83	596	601	606	611	616	621	626	630	635	640	
84	645	650	655	660	665	670	675	680	685	689	
85	694	699	704	709	714	719	724	729	734	738	
86	743	748	753	758	763	768	773	778	783	787	
87	792	797	802	807	812	817	822	827	832	836	
88	841	846	851	856	861	866	871	876	880	885	
89	890	895	900	905	910	915	919	924	929	934	
890	939	944	949	954	959	963	968	973	978	983	
91	988	993	998	*002	*007	*012	*017	*022	*027	*032	
92	95 036	041	046	051	056	061	066	071	075	080	
93	085	090	095	100	105	109	114	119	124	129	
94	134	139	143	148	153	158	163	168	173	177	
95	182	187	192	197	202	207	211	216	221	226	
96	231	236	240	245	250	255	260	265	270	274	
97	279	284	289	294	299	303	308	313	318	323	
98	328	332	337	342	347	352	357	361	366	371	
99	376	381	386	390	395	400	405	410	415	419	
900	424	429	434	439	444	448	453	458	463	468	
N	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**P P**

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7	4.2
8	4.8
9	5.4

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3	1.5
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7	3.5
8	4.0
9	4.5

	4
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2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6

TABLE I.—COMMON LOGARITHMS OF NUMBERS
To Five Decimal Places

N	0	1	2	3	4	5	6	7	8	9	PP
900	95 424	429	434	439	444	448	453	458	463	468	
01	472	477	482	487	492	497	501	506	511	516	
02	521	525	530	535	540	545	550	554	559	564	
03	569	574	578	583	588	593	598	602	607	612	
04	617	622	626	631	636	641	646	650	655	660	
05	665	670	674	679	684	689	694	698	703	708	
06	713	718	722	727	732	737	742	746	751	756	
07	761	766	770	775	780	785	789	794	799	804	
08	809	813	818	823	828	832	837	842	847	852	
09	856	861	866	871	875	880	885	890	895	899	
910	904	909	914	918	923	928	933	938	942	947	
11	952	957	961	966	971	976	980	985	990	995	
12	999	*004	*009	*014	*019	*023	*028	*033	*038	*042	
13	96 047	052	057	061	066	071	076	080	085	090	
14	095	099	104	109	114	118	123	128	133	137	
15	142	147	152	156	161	166	171	175	180	185	
16	190	194	199	204	209	213	218	223	227	232	
17	237	242	246	251	256	261	265	270	275	280	
18	284	289	294	298	303	308	313	317	322	327	
19	332	336	341	346	350	355	360	365	369	374	
920	379	384	388	393	398	402	407	412	417	421	
21	426	431	435	440	445	450	454	459	464	468	
22	473	478	483	487	492	497	501	506	511	515	
23	520	525	530	534	539	544	548	553	558	562	
24	567	572	577	581	586	591	595	600	605	609	
25	614	619	624	628	633	638	642	647	652	656	
26	661	666	670	675	680	685	689	694	699	703	
27	708	713	717	722	727	731	736	741	745	750	
28	755	759	764	769	774	778	783	788	792	797	
29	802	806	811	816	820	825	830	834	839	844	
930	848	453	858	862	867	872	876	881	886	890	
31	895	900	904	909	914	918	923	928	932	937	
32	942	946	951	956	960	965	970	974	979	984	
33	988	993	997	*002	*007	*011	*016	*021	*025	*030	
34	97 035	039	044	049	053	058	063	067	072	077	
35	081	086	090	095	100	104	109	114	118	123	
36	128	132	137	142	146	151	155	160	165	169	
37	174	179	183	188	192	197	202	206	211	216	
38	220	225	230	234	239	213	248	253	257	262	
39	267	271	276	280	285	290	294	299	304	308	
940	313	317	322	327	331	336	340	345	350	354	
41	359	364	368	373	377	382	387	391	396	400	
42	405	410	414	419	424	428	433	437	442	447	
43	451	456	460	465	470	474	479	483	488	493	
44	497	502	506	511	516	520	525	529	534	539	
45	543	548	552	557	562	566	571	575	580	585	
46	589	594	598	603	607	612	617	621	626	630	
47	635	640	644	649	653	658	663	667	672	676	
48	681	685	690	695	699	704	708	713	717	722	
49	727	731	736	740	745	749	754	759	763	768	
950	772	777	782	786	791	795	800	804	809	813	
N	0	1	2	3	4	5	6	7	8	9	PP

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3	1.5
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8	4.0
9	4.5

	4
1	0.4
2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6

TABLE I.—COMMON LOGARITHMS OF NUMBERS

To Five Decimal Places

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	
51	818	823	827	832	836	841	845	850	855	859	
52	864	868	873	877	882	886	891	896	900	905	
53	909	914	918	923	928	932	937	941	946	950	
54	955	959	964	968	973	978	982	987	991	996	
55	98 000	005	009	014	019	023	028	032	037	041	
56	046	050	055	059	064	068	073	078	082	087	
57	091	096	100	105	109	114	118	123	127	132	
58	137	141	146	150	155	159	164	168	173	177	
59	182	186	191	195	200	204	209	214	218	223	
960	227	232	236	241	245	250	254	259	263	268	
61	272	277	281	286	290	295	299	304	308	313	
62	318	322	327	331	336	340	345	349	354	358	
63	363	367	372	376	381	385	390	394	399	403	
64	408	412	417	421	426	430	435	439	444	448	
65	453	457	462	466	471	475	480	484	489	493	
66	498	502	507	511	516	520	525	529	534	538	
67	543	547	552	556	561	565	570	574	579	583	
68	588	592	597	601	605	610	614	619	623	628	
69	632	637	641	646	650	655	659	664	668	673	
970	677	682	686	691	695	700	704	709	713	717	
71	722	726	731	735	740	744	749	753	758	762	
72	767	771	776	780	784	789	793	798	802	807	
73	811	816	820	825	829	834	838	843	847	851	
74	856	860	865	869	874	878	883	887	892	896	
75	900	905	909	914	918	923	927	932	936	941	
76	945	949	954	958	963	967	972	976	981	985	
77	989	994	998	*003	*007	*012	*016	*021	*025	*029	
78	99 034	038	043	047	052	056	061	065	069	074	
79	078	083	087	092	096	100	105	109	114	118	
980	123	127	131	136	140	145	149	154	158	162	
81	167	171	176	180	185	189	193	198	202	207	
82	211	216	220	224	229	233	238	242	247	251	
83	255	260	264	269	273	277	282	286	291	295	
84	300	304	308	313	317	322	326	330	335	339	
85	344	348	352	357	361	366	370	374	379	383	
86	388	392	396	401	405	410	414	419	423	427	
87	432	436	441	445	449	454	458	463	467	471	
88	476	480	484	489	493	498	502	506	511	515	
89	520	524	528	533	537	542	546	550	555	559	
990	564	568	572	577	581	585	590	594	599	603	
91	607	612	616	621	625	629	634	638	642	647	
92	651	656	660	664	669	673	677	682	686	691	
93	695	699	704	708	712	717	721	726	730	734	
94	739	743	747	752	756	760	765	769	774	778	
95	782	787	791	795	800	804	808	813	817	822	
96	826	830	835	839	843	848	852	856	861	865	
97	870	874	878	883	887	891	896	900	904	909	
98	913	917	922	926	930	935	939	944	948	952	
99	957	961	965	970	974	978	983	987	991	996	
1000	00 000	004	009	013	017	022	026	030	035	039	
N	0	1	2	3	4	5	6	7	8	9	P P

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7	3.5
8	4.0
9	4.5

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2	0.8
3	1.2
4	1.6
5	2.0
6	2.4
7	2.8
8	3.2
9	3.6

AUTHOR INDEX

SUBJECT INDEX