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METALLURGICAL ANALYSIS

BY

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PREFACE TO THE FIFTH EDITION

The fifth edition of Metallurgical Analysis has been made necessary by the rapid development of control and testing methods in the industrial, and especially the metallurgical, world in the past seven years. The author has been actively engaged during this period in metallurgical testing both as a teacher and as a consulting metallurgist and has been forced to recognize the desirability of a complete revision.

In this revision the old material has been largely rewritten. The chapters on coal calorimetry, gas calorimetry, fire assaying and electrometric titration are entirely new. The chapters on water analysis, analysis of alloy steels and gas analysis have been almost entirely rewritten. Nearly all of the methods described in these and other chapters have been used many times in the author's private laboratory by experienced analysts and in the student laboratories as well. The author feels, therefore, a good deal of confidence in the practical usefulness of this new edition.

The scope of these methods has been enlarged to include insofar as possible all of the chemical analyses which the metallurgical chemist is likely to require except those of paint. The earlier editions of this book have been widely used in the works' laboratories and in college metallurgical laboratories where a bulky text is not altogether desirable. For this reason explanatory matter concerning the fundamental principles of analytical chemistry, use and care of balances, calibration of instruments and the principles and methods of stoichiometry is not included in the text. A statement of a few of the fundamental principles is, however, given on page xii for convenience reference.

The author wishes to express his appreciation of the help received from his brother, F. M. Demorest, through whose careful and accurate analytical work so many of the methods described in this book have been tested.

D. J. DEMOREST.

June, 1924.

PREFACE TO THE FIRST EDITION

These notes were written for the use of the writer's students in the metallurgical laboratory of the Ohio State University.

The object was to give in a condensed form the series of selected methods in metallurgical analysis which made up the course of study.

To the descriptions of the processes, such explanations have been added as experience has shown to be desirable for the assistance of the student in understanding the conditions necessary for accurate results.

Such methods only are given as have been tested by repeated use in the laboratory and found satisfactory.

No attempt is made to describe general reagents or apparatus, as students prepared to take this course are always familiar with all ordinary laboratory equipment, and for special forms of apparatus reference is made to easily accessible books and papers.

The writer wishes to acknowledge his obligation to Blair, Troilius and other standard writers, as well as to numerous papers in the various technical and scientific journals, though it has been impossible to give credit in detail to all the sources from which material was taken in compiling these notes.

The references added are only those which it seemed important the student should consult for fuller information on the subject.

N. W. LORD.

October 28, 1893.

INTRODUCTION

Before beginning the course in special analysis given in these notes, the student is supposed to be familiar with the ordinary qualitative reactions of the acids and bases, the preparation of reagents, and so much of the general methods of quantitative analysis as includes the use of the balance and weights, the ordinary operations of filtration, washing, drying, igniting, and weighing of precipitates, the evaporation of solutions, and also the use and calibration of graduated glassware.

A careful study of the first two sections of Fresenius's "System of Quantitative Analysis," the first 40 pages of Treadwell-Hall's "Analytical Chemistry," Vol. 2, the first two chapters of "A Treatise on Quantitative Inorganic Analysis," by Mellor, and especially Foulk's "Quantitative Analysis," Part 1, is advisable in regard to all these points of manipulation.

In addition to the above a few general precautions and explanations are necessary and should never be overlooked.

In adding reagents to produce any given effect it is important that the right amount be used. To determine what this will be demands a thorough knowledge of what is to take place. In the descriptions of the various processes these amounts are approximately indicated, but it is impossible to provide in this way for all contingencies. Therefore, if the amount of reagent directed fails to do the work it must be increased or diminished as may appear necessary. Thus in every case where a precipitate is formed, it is *essential* that the filtrate be tested by a further addition of the reagent to make sure that the precipitation is complete. This is best done by adding the reagent to a small portion of the liquid in a test-tube, and if a precipitate forms, returning this to the main volume; often a little of the clear liquid over the precipitate can be tested in this way before filtration.

The purity of the reagents, even if marked "c.p.," should always be tested. In many cases it is necessary to run a "blank" determination by going through the process with the reagents alone, leaving out the substance to be tested. The amount of any impurity which would affect the result can be thus determined and allowed for.

A process should be tested by repeated determinations made on different amounts of the substance. Agreement of the results in this case is a better indication of accuracy than if the same amounts are taken in each determination. Also each process must be tested on material of known composition, such as the Government standards. Every laboratory should have these standards. This cannot be too strongly insisted upon.

The amounts of material prescribed in the descriptions of the processes are those most generally used. They may be changed provided the amounts of the reagents be varied to correspond.

In many of the processes the calculations may be greatly simplified by taking "factor weights" of the material instead of even grams. This consists in weighing out an amount of the substance equal to the fraction that the material to be determined forms of the precipitate weighed. When this is done the weight of the precipitate in grams multiplied by 100 will give directly the percentage sought. If the factor weight is inconveniently large or small some simple multiple of it can be taken and the result estimated accordingly.

For example: 1 gram of $BaSO_4$ contains 0.137 gram S, and if ten times this factor (1.37 grams) of any substance is taken for the determination of sulfur, each milligram of $BaSO_4$ obtained represents 0.01 per cent of sulfur. A table of convenient factors of this kind is added at the end of this book and the weights there given may be used, when desirable, in place of those directed in the processes.

A similar method is often used in weighing out material for volumetric determinations when a standard solution is used of which the value of 1 c.c. is determined experimentally and is not an aliquot part of a gram. For illustration see directions for the volumetric determination of lime, page 25.

Every chemist should have a good microscope in his laboratory and use it frequently, especially when unusual or strange material is sent to him for analysis. This will be a great help in showing him the nature of the material and will prevent him from wasting time on useless determinations and from omitting those that ought to be made. The microscope should have the proper attachment for studying material under polarized light. For metal examination the microscope should have provision for illuminating the object with vertical illumination.

The methods of analysis given in this book are of as universal application as possible. When a large number of determinations of a certain kind are made in a laboratory, the details of manipulation can be arranged so as to save much time and expense. For an exhaustive discussion of this subject see RIDSDALE, "Mechanicalizing Analysis as an Aid to Accuracy and Speed for Commercial Purposes," *J. Iron Steel Inst.* (1911), no. 1, pp. 332–375, and *Proc.* Cleveland Inst. of Eng. (1911–1912), no. 4, p. 149.

The acids and ammonium hydroxide solution used in this book are, unless otherwise stated, of the following specific gravities:

Hydrochloric acid	1.19
Nitric acid	1.42
Sulfuric acid	1.84
Ammonium hydroxide	0.90

The analyst must always take care to assure the accuracy of his balances, weights, burettes and all measuring apparatus by calibrating them carefully, checking his work by using U. S. Bureau of Standards certificates.

It is impossible in a text of this size to state and explain satisfactorily the fundamental principles of analytical chemistry and to illustrate them with examples and problems. It is expected that the teacher using this text will amplify the notes given with each analytical procedure by pointing out the application of the laws of physics and chemistry to the process under discussion. It is quite essential that students be required to work and hand in, in neat and satisfactory form, a large number of problems in which the quantitative relationships of each analytical process are involved. In this way only can an active appreciation of quantitative chemistry be obtained. It has been thought that the inclusion of a large number of problems in the text would add too much to the size of the volume. At any rate, a teacher who is qualified to handle metallurgical analysis would also be quite capable of easily devising an ample number of problems for his students.

A good many years of experience, both as a practising metallurgical chemist in private and metallurgical plants and as a teacher of Metallurgy, including metallurgical analysis, has given the writer a pretty fair knowledge of the needs of the metallurgical student and the metallurgical chemist in a works laboratory. The writer knows how easy it is for both the student in metallurgical engineering and the metallurgical chemist to forget the fundamentals which he has previously learned. Hence, a few of the fundamental laws are briefly given below so that the student can easily refer to them when the teacher is explaining the principles involved in the processes of analysis given in the book and so that the works chemist can refresh his memory when necessary.

Boyle's Law for Gases.—At a constant temperature the volume of a given quantity of any gas varies inversely as the pressure to which the gas is subjected. This idea is expressed in the following formulas:

$$PV = \text{a constant, or } P = \frac{1}{V}, \text{ or } V = \frac{1}{P}, P, \text{ or } PV = P_1V_1.$$

Dalton's Law of Partial Pressures.—The pressure exerted by a mixture of gases is equal to the sum of the separate pressures which each gas would exert if it alone occupied the whole volume. This fact is expressed in the following formula:

$$PV = V(p_1 + p_2 + p_3, \text{ etc.})$$

Faraday's Law.—The amounts of decomposition effected by the passage of equal quantities of electricity through electrolytes are, for the same electrolyte, equal, and for different electrolytes are proportional to the combining weights of the elements or radicals which are deposited.

Gay-Lussac's Law for Gases (or Charles' Law).—At a constant pressure, the volume of a given quantity of any gas increases about $\frac{1}{273}$ of its volume at 0°C. for each rise of 1°C., and at constant volume the pressure of a given quantity of any gas increases about $\frac{1}{273}$ of the pressure at 0°C. for each rise of 1°C. in temperature. The volume of a gas is proportional to its absolute temperature.

Hess's Law of Constant Heat Summation.—The amount of heat generated by a chemical reaction is the same whether reaction takes place in one step or in several steps, or all chemical reactions which start with the same original substances liberate the same amounts of heat, irrespective of the process by which the final state is reached.

Henry's Law.—The amount of gas which a liquid will dissolve is directly proportional to the pressure of the gas. This holds for all gases which do not unite chemically with the solvent.

The Law of Mass Action.—At a constant temperature the product of the active masses on one side of a chemical equation when divided by the product of the active masses on the other side of the chemical equation is a constant, regardless of the amounts of each substance present at the beginning of the action. The law of mass action can be expressed in the following form:

$$m_1A_1 + m_2A_2 + m_3A_3 + \dots = n_1B_1 + n_2B_2 + n_2B_3 + \dots,$$

then equilibrium will exist when the concentration a_1, a_2, a_3 . . . b_1, b_2, b_3, . . . of the reacting substances have acquired certain values. These values are given by the following equation:

$$\frac{a_1^{m_1} \cdot a_2^{m_2} \cdot a_3^{m_3} \cdots}{b_1^{n_1} \cdot b_2^{n_2} \cdot b_3^{n_3} \cdots} = k.$$

The Periodic Law.—The physical and chemical properties of the elements are functions of their atomic weights, and the most of these properties are periodic functions of the atomic weights.

The Phase Rule of Gibbs.—A system consisting of C components can exist in $C + 2$ phases only when the temperature, pressure and concentration have fixed and definite values; if there are C components in $C + 1$ phases, equilibrium can exist while one of the factors varies, and if there are only C phases, two of the varying factors may be arbitrarily fixed. This rule may be very concisely and conveniently summarized in the form of the equation:

$$P + F = C + 2, \text{ or } F = C + 2 = P$$

where P denotes the number of phases, F the degrees of freedom and C the number of components.

The Electrolytic Dissociation or Ionization Theory.—When an acid, base or salt is dissolved in water or any other dissociating solvent, a part or all of the molecules of the dissolved substances are broken up into parts called ions, some of which are charged with positive electricity and are called cations, and an equivalent number of which are charged with negative electricity and are called anions.

Electrolytic Solution Tension Theory (or the Helmholtz Double Layer Theory).—When a metal, or any other substance capable of existing in solution as ion, is placed in water or any other dissociating solvent, a part of the metal or other substance passes into solution in the form of ions, thus leaving the remainder of the metal or substance charged with an equivalent amount of electricity of opposite sign from that carried by the ions. This establishes a difference in potential between the metal and the solvent in which it is immersed.

The Theorem of Le Chatelier.—If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, *i.e.*, one by which its effect is partially annulled.

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METALLURGICAL ANALYSIS

CHAPTER I

THE SELECTION AND PREPARATION OF SAMPLES FOR ANALYSIS

General Principles.—The object sought by the technical analyst is to ascertain the average composition of some particular lot of material—for example, a carload of ore, an ingot of metal or a bin full of coal.

The amount of material treated in the laboratory is of necessity limited to a few grams. The preparation of this small portion so that its analysis shall correctly represent the composition of the mass from which it is taken constitutes the operation of "*sampling.*"

The general mode of procedure is to take from the mass in question several portions selected from different points, and containing coarse and fine material in as nearly as possible the same proportion as they exist in the mass as a whole. This large sample which may weigh from a fraction of a pound to a ton, according to the amount of material the chemist has to examine, as well as to the *extent of variation permissible in the results*, is then crushed to ½ in. or smaller, thoroughly mixed and subdivided by "quartering," until a sample of about 10 lb. is obtained. This is pulverized and all put through a 6-mesh sieve, well mixed and again subdivided, till a sample of 100 to 300 grams is obtained, which is put through an 80- to 100-mesh sieve and bottled for use.

The operation of "quartering" is conducted as follows: The material after being well mixed by shoveling is formed into a pile which is then flattened out by a spiral motion of the shovel. This pile is then divided into four quarters by cutting across at right angles.

Two diagonally opposite quarters are selected and the intermediate ones removed. Care should be taken to brush away carefully all the material of the rejected quarters. The two remaining ones are then mixed together and the operation repeated until a sufficient reduction in bulk is made.

However, if the apparatus is available, it is best to perform the quartering mechanically by a riffle sampler or an apparatus like the Foster-Coolidge automatic sampling machine, especially if many large samples are to be handled. These automatic samplers are more accurate than the hand quartering and much more rapid.

The errors in sampling may be many times larger than those of the chemical analysis, and it is necessary for the chemist to supervise strictly the sampling of the materials which he is to analyze. Otherwise the value of his work may be greatly reduced because of the sample being non-representative of the material it is supposed to represent.

The errors in sampling may be due to faulty methods of taking the sample as, for instance, taking one or several lumps of ore or coal from a carload when the carload is composed of materials of different composition. Further, it may be very difficult to secure a correct sample because of the heterogeneous composition of the material and the irregular distribution of the different materials of the shipment. Thus, coal is contaminated with slate and pyrite which may be very unevenly distributed. In the sampling of metals the great sources of error are due to segregation of the components of the metal and contamination of the sample with metal and oil from the drill.

In sampling minerals, as coal and iron ore, it is necessary for the sampler to keep in mind the importance of the "size weight" ratio. That is, it is necessary to maintain the sample at all times so large that the loss or gain of a lump as large as the largest lump in the sample and of whatever composition would not affect the accuracy of the sample noticeably. Further, it is necessary that, in quartering the sample, the sample be kept crushed so fine that the gain or loss of the largest lump present, of whatever composition, will not noticeably affect the sample. In other words, it is necessary that the sampler be a man of intelligence and that he use his intelligence in sampling.

Many variations from the general procedure will be necessary with different materials. The following general principles may be stated as a guide:

1. As to the size of the original large sample. This must be greater as the material is less homogeneous and as the importance of the exact determination of any ingredient increases. Thus, a limestone can easily be sampled; but a gold or silver ore consisting of small, detached fragments of a very valuable material in a valueless rock may require the fine crushing of the whole mass of ore and its careful mixing and subdivision, to secure an "average assay."

2. Materials of decidedly different specific gravities require great care to prevent separation into layers during mixing. (Quartering constitutes a fair safeguard against this source of error.)

3. When the ore is sifted, every particle must go through the sieve. The harder parts, which are left unbroken till the last, are often of different composition from the softer and first pulverized portions, and if rejected would cause serious error.

4. Certain ores and slags contain particles of metal which cannot be pulverized. In this case the grains of metal not passing through the sieve must be collected and weighed. The portion passing through the sieve is also weighed. The metal and the siftings are then analyzed separately, and the two analyses combined in the ratio of the relative weights.

Sampling of Metals.—The sampling of metals presents many difficulties. Melted metals can be sampled during pouring by taking a little at the beginning, middle and end of the cast, and averaging the three analyses.

In general it may be stated:

1. Cast ingots are *not* homogeneous. Drillings from different portions will show different analyses. Hence, drillings from a number of points must be well mixed. A single "pig" of cast iron may vary largely in composition from top to bottom.

2. In tapping a mass of metal from a furnace, different portions of the "run" will show differences in composition. Thus, a "bed" of pig iron will show wide variations in silicon and sulfur between the top and bottom of the cast.

3. In some metals the operation of drilling will result in a separation; for example, in drilling pig iron, the fine portion will be of different composition from the coarse; hence, careful mixing of the drillings is necessary.

WEIGHING OUT FROM THE LABORATORY SAMPLE

In this operation the tendency of materials of different specific gravity to separate must never be lost sight of. The substance should be carefully mixed upon a sheet of glazed paper and small portions taken from different parts.

A second source of error is the separation of coarse and fine, as in metal drillings. Great care is necessary to avoid serious difficulty here. The drillings may be moistened with alcohol to make them adherent, and then small portions may be separated, to be subsequently accurately weighed when dry (SHIMER).

Dirty pig-iron samples are frequently sent to the chemist, the drillings being contaminated by sand, wood, grease, etc. These may be cleaned from sand with a magnet and from grease by washing with ether, but the analytical results on such samples should never be regarded as entirely satisfactory.

ESTIMATION OF MOISTURE

Many materials (ores, clays, limestones, etc.) as sampled in bulk are often too damp to pulverize. Such samples must be dried on a steam bath or by other means, and the loss of weight determined. The weighing can be done on a portion of the crushed and mixed material which, after drying, is added to the rest of the air-dry sample. It is also always well to determine moisture in the final sample, and allow for it if present. The temperature for drying must not much exceed 100°C., or water of composition may be expelled.

The analysis may be stated on the "dry basis," but should also be calculated on the basis of the wet material.

For example, a cargo of iron ore was sampled in the vessel while unloading, as follows: After the bottom of the boat was reached, portions of the ore were taken every 18 in. from the top to the bottom of the sloping sides of the ore exposed in the hold, including lump and fine in the proportions they formed at each point. This was repeated when the vessel was about half unloaded. The total amount taken was 200 lb. This was broken up as fine as beans, well mixed by shoveling and divided by quartering until a portion of 10 lb. was obtained, all being done rapidly to avoid loss of moisture.

Weight	9,254 grams
After drying in a pan on a steam boiler, weight	8,649 grams
Loss	605 grams

This was then pulverized and mixed, and a portion of 100 grams taken for the laboratory. This assayed—

Iron	58.4 per cent

Then 9,254 : 8,649 = 58.4 : 54.6 = the per cent of iron in the ore in its original condition.

It may be noted, first, that many ores will absorb water during the pulverization (the amount of water so absorbed will vary with the weather); second, complete drying of a large sample is very difficult; third, ordinary corked bottles are not moisture-proof, and samples left in such will change in the course of time, if they are hygroscopic.

In the case of coal, especially the "dry" or non-coking coals and lignites, sampling so as to preserve the moisture in the material unaltered presents many difficulties. Such coals, when pulverized, rapidly lose moisture in dry air at ordinary temperatures, and if then exposed to moist air, partially regain it.

The original sample should be rapidly crushed and quartered down, avoiding all unnecessary exposure to air. The final sample can be preserved in rubber-sealed "fruit jars."

In preparing the small fine sample for analysis, speed and covered sieves are necessary. The pulverized material must be kept in bottles with rubber stoppers.

Wet samples, such as coal from a "washer," may be air dried at room temperatures until they can be pulverized, but will not then show, as a rule, the same moisture as the original coal before wetting; hence, if this coal is to be compared with the coal before washing, that should be similarly air dried.

Where much work is done, special ovens for drying samples are of great assistance.

A wooden or cement floor is desirable for quartering large samples, but rubber or oilcloth spread out on the ground can be used.

It should never be forgotten that in grinding hard material with metallic apparatus more or less of the metal will go into the product. Thus, a sample of blast-furnace slag ground in an iron mortar would show more iron than was actually in the slag; therefore, for the accurate determination of a small amount of iron in such a material, a special sample crushed in agate should be prepared.

Sampling Coal.—In sampling coal as it is unloaded from a car or boat small portions should be taken at regular intervals during unloading. The total amount will vary according to the nature of the coal. Of fine slack, about 200 lb. from a car will be sufficient, while if the coal is lump, 500 or 1,000 lb. will be necessary. If a number of cars are to be sampled and the analysis of the mixed samples is to be made, a much smaller amount may be taken from each car.

The entire sample should be spread out on a floor and the larger pieces broken with a hammer, unless a power crusher is handy when the entire lot is put through the crusher. The crushed sample is then well mixed and quartered by hand or by a sampling machine and the crushing and dividing repeated until a sample small enough to send to the chemical laboratory is obtained. If the sample has been crushed as small as ⅛ in., the amount sent to the laboratory need not be larger than 5 lb.

The laboratory sample when received is weighed and thoroughly air dried by exposing in a warm room for about 36 hours or by drying in a drier heated about 10° above the room temperature and with a rapid circulation of air. The sample is then weighed, and the drying continued a half day if mere air drying is done, or two hours if the drier is used. The sample is weighed again and, if a loss of not more than 0.2 per cent is found, the drying has been sufficient. The air-drying loss is then calculated in per cent.

The dried sample is then crushed to about 8 mesh and quartered to a pound. It is again crushed to 10 mesh and quartered to ½ lb., and this is then ground on a bucking board or, better, in a ball mill until it will go through a 60-mesh sieve. A 2-oz. sample is then put in a rubber-stoppered sample bottle and it is ready for analysis.

The entire sampling, both before and after air drying, must be done as quickly as possible to prevent loss or gain of moisture during the sampling. The sample should not be ground finer than 60 mesh, as it then takes up oxygen rapidly. A coarse sample which has been well air dried may lose as much as a per cent of moisture on being exposed to the air a few minutes after fine grinding. The fine sample must be analyzed promptly, even if well stoppered, as it alters rapidly by oxidation and moisture changes.

If the large sample of several hundred pounds first taken is wet or damp it should be weighed and spread out on a floor until dry and weighed again before any quartering is done.

Channel Sampling a Seam of Coal.—The details of taking and preparing an average channel sample are as follows: The vertical face of the coal is thoroughly cleaned, if necessary, and the proposed sample is marked out by drawing two parallel vertical lines, spaced 6 in. apart, from the top to the bottom of the coal measure to be mined. A strong canvas cloth is placed beneath the area thus marked off, and spread upon the mine floor to receive the sample, which is procured with a pick by cutting the coal, starting preferably at the bottom, from between the two parallel lines to a uniform depth of 2 in. The canvas is now doubled over the sample thus collected, and all the larger lumps broken by blows from the side of the pick. The sample is then preferably transferred to a steel or iron plate for the crushing and quartering operations. Before the first quartering, the entire sample is reduced to pass a ½-in. screen, after which the two quarters retained are further reduced to pass a ¼-in. screen. The second half retained may now be quartered down to approximately 10 lb. without any further crushing. This 10-lb. sample is either crushed to pass a 10-mesh sieve before further quartering can be done, or it is sent to the laboratory for the final preparation, which is carried out as described later under the heading "Laboratory Preparation of Samples."

In order to locate troublesome impurities, it is advantageous to remove the channel sample in sections. In this case the sections are measured, their lengths recorded and the sample from each section of the whole channel is kept separate and treated as described for the average channel sample. Since each section makes up a definite part of the whole channel, the average composition of the entire channel sample can readily be calculated after the individual sections have been analyzed.

As the composition of the coal mined from a bed is liable to change suddenly, the frequency with which channel samples are taken is important. If the purpose for which the coal is being mined requires accurate prior knowledge as to its average composition, not fewer than three channel samples should be taken in well-developed workings for every 100 wagons of output.

Sampling Iron Ores.—The principles are the same as for coal. It is always best to sample the lot as it is being loaded or unloaded, since the material on top may be of different composition from that underneath. At stated intervals of time a shovelful is taken. Or after the ore has been partially removed from the boat or car, leaving cone-shaped depressions, the samples are taken from the faces of these depressions. Thus, after a grab has removed as much ore as possible from a hatch, the sampler goes to the face of the cone and, starting from the bottom, he takes trowel samples at stated intervals in a straight line up one side of the cone. This he repeats in four different directions, starting each time from the bottom of the cone. The entire sample from a boat may weigh 1,000 lb.

In sampling cars sometimes a rope net is spread over the car and a sample of several ounces is taken from underneath each knot of the net, of which knots the net will have about 36. The same thing can be done without the net. The ore should not be taken from the surface, but from far enough underneath to get beyond the reach of surface wetting or evaporation. But it is always best to get the sample from the car while unloading so as to get samples all through the mass of ore.

The sample is weighed, if wet, and dried, if not too large, on a steam pan or in a drying oven at 100° and weighed again. This gives the drying loss. It is then crushed to ½-in. size or smaller and divided, crushed smaller and again divided, until the sample weighs about 5 lb. and is about ⅛-in. mesh size. This is dried at 100°C. to constant weight, and the loss in weight calculated in per cent. The sample is quartered to about a pound and then ground to 100 mesh in a disc pulverizer having manganese steel discs, or in a ball mill, or on a manganese steel bucking board. The sample is then mixed well and quartered in a small riffle sampler to about 100 grams and bottled in a rubber-stoppered bottle.

If the original sample is wet and too large to be dried conveniently, 100 lb. are accurately weighed and dried at 100°C. for 18 hours and weighed again, and the dry ore added to the rest of the sample, which is then treated as above directed. If 100 lb. is too large for the drier, 25 lb. may be taken.

References on Iron Ore Sampling:

- Wiley, "Methods used at Illinois Steel Co.," *J. Ind. Eng. Chem.*, **3**, 103.
- *J. Anal. App. Chem.*, **5**, 299.
- Glenn, *Trans.* Am. Inst. Min. Eng., **20**, 155.
- Landis, *Trans.* Am. Inst. Min. Eng., **20**, 611.
- Kiddie, "Causes of Errors," *Eng. Mining J.*, **88**, 824.
- U. S. Steel Corporation, "Methods for the Commercial Sampling and Analysis of Iron Ores."

References on Coal Sampling:

- Somermeier, "Coal," pp. 57–79.
- Bailey, *J. Ind. Eng. Chem.*, **1**, 161.
- U. S. Steel Corporation, "Sampling and Analysis of Coal, Coke and By-products."

Sampling of Pig Iron.—When the iron is run out of the furnace, a spoonful is taken several times during the cast, at least once at the beginning, once at the middle of the cast and once near the end. If the iron is run into ladles, it is well to take spoonful from the middle of each ladleful. The spoonfuls of metal are poured into cast-iron molds about 10×4×3 in. outside dimensions and with inside dimensions of about 6×1¾×1¼ in. deep, with a projection in the center so that the ingot will have a notch in order that it may be easily broken to observe the fracture. The ingot should be drilled deeply in at least two places to get drillings for analysis. The drillings from all the ingot samples from a cast are mixed for analysis.

The drill must be worked *dry* (without oil) and care should be taken to reject the outer "skin" of the ingot or bar, which usually contaminated with matter not properly belonging in the analysis. Cast iron is frequently sampled by pouring a little of the molten metal into water. This makes the iron white and very brittle. These so-called "shot samples" and similar brittle material, as "spiegel iron" and "wash metal," which are too hard to drill, must be broken into small fragments with a sledge hammer and several pieces pulverized in a steel mortar. A very efficient mortar for this purpose can be made by boring a hole 2 in. deep and 1 in. in diameter into a block of tool steel about 3 in. square and 4 in. high. Fit this with a steel "rammer" cut from a round bar and about 3 in. longer than the hole. It must be only slightly smaller than the hole in the block. Both block and rammer must be well hardened. By dropping a fragment of metal into the hole, inserting the rammer and pounding it vigorously with a heavy hammer, the hardest material is soon reduced to a fine sand.

In sampling all metal ingots and billets it must be remembered that the metal will vary in composition from place to place because of segregation, and so must be drilled in several places and if possible clear through.

REFERENCES ON SAMPLING METALS:

SHIMER, *Trans.* Inst. Min. Eng., **14,** 760.

KELLER, "Copper Bar Sampling," *Eng. Mining J.*, **93,** 703.

U. S. Steel Corporation, "Methods used by the Chemists of—for Sampling and Analysis of Pig Iron."

Sampling Equipment.—The following or similar equipment is necessary in any laboratory which does a large amount of work:

1. A drill press, preferably a power drill press.

2. A swing hammer pulverizer equipped with a chute for mechanically dividing the samples. The Jeffrey "baby pulverizer," made by the Jeffrey Manufacturing Company of Columbus, Ohio, has a capacity of 1,000 lb. of coal per hour reduced to ¼ in. It uses about 7 hp.

3. A hand or power jaw crusher is especially useful for crushing hard rock, but is also satisfactory for coal crushing to about ¼ in. The "Chipmunk" crusher, made by the Braun Corporation of Los Angeles, will crush 200 lb. per hour to ¼-in. size in the small crusher and 1,000 lb. per hour in the large size. About 2 [illegible]. is required.

4. A pair of 6-in. rolls is needed to crush from ¼-in. size to 10 mesh. The 6-in. rolls made by the American Concentrator Company of Joplin, Mo., can reduce fifty to one hundred 4-lb. samples from ¼ in. to 10 mesh in a day.

5. For reducing the 10-mesh coal samples to 60 mesh or finer a pebble ball mill is very efficient, especially as it prevents moisture changes during the grinding. A four-jar mill, such as the one made by The Abbé Engineering Company of New York, will grind forty to fifty samples per day if extra jars are provided.

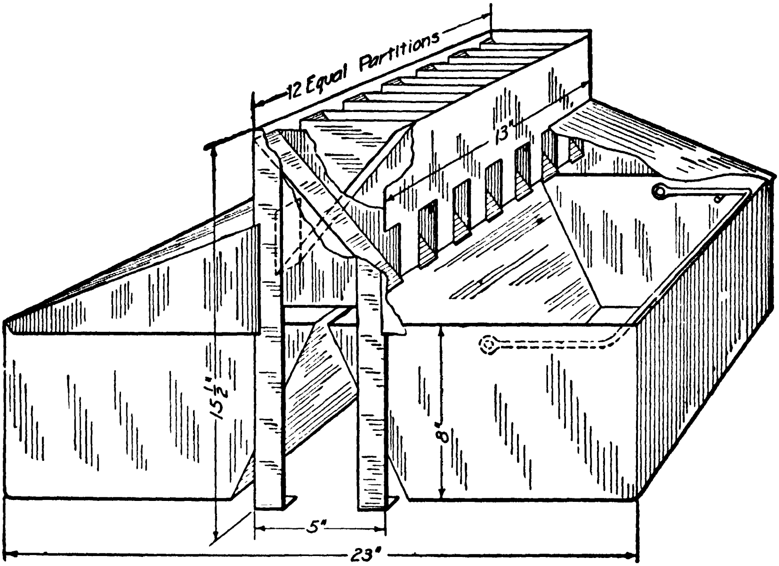

Fig. 1.

6. For occasional sampling a bucking board with heavy muller answers the purpose of fine grinding any mineral sample. It is best made of manganese steel or chrome steel. These steels are so hard that they wear very slowly.

7. A mechanical divider such as the Foster-Coolidge machine is almost a necessity when large numbers of large samples are handled. For samples weighing less than 100 lb. the riffle sampler shown in Fig. 1 answers all purposes, unless a large number of samples are handled.

8. Coarse wooden frame sieves from 1 to ¼ in. and brass sieves from 10 to 120 mesh are necessary in the sampling room.

9. For fine grinding of ores an Iler or other disc pulverizer is indispensable if many samples are to be ground.

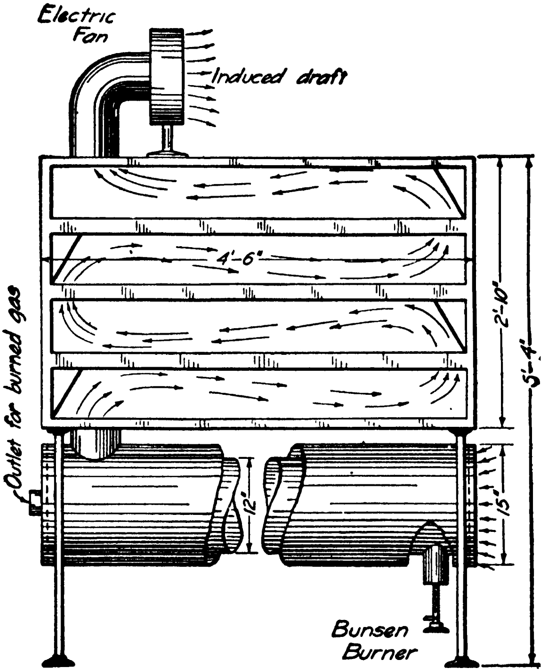

Fig. 2.

10. For drying coarse ores, and especially coals, the oven shown in Fig. 2 is convenient. A steam-heated pan or table is also useful, especially for wet ores.

11. A large platform scale for weighing up to 1,000 lb. and a Troemner solution scale No. 80 for weighing up to 5 lb. are necessary.

CHAPTER II

THE ANALYSIS OF LIMESTONES

The constituents to be determined are silica, oxide of iron, oxide of aluminium, carbonate of calcium and carbonate of magnesium. The silica is present chiefly as quartz, clay and other silicates. Besides oxide, iron may be present as ferrous carbonate, or combined with sulfur as pyrite. Small amounts of phosphoric acid and sulfates are also often present, and are determined as in iron ores. Since the water combined in the clay and other constituents such as organic matter are not determined, the results will usually not total up to 100 per cent.

In examining limestone quarries to determine the quality of the stone for furnace flux, lime or cement manufacture, the rock should be sampled layer by layer, as different layers usually vary greatly from each other in composition, while material from the same layer (or "bed") is likely to be of uniform composition. The stone generally ranks in quality according to the carbonate of lime. For fluxing purposes it must be as free from silica as possible.

The procedure for analysis in outline is as follows: The sample is dissolved in HCl; silica is rendered insoluble by dehydration and filtered off; $Fe(OH)_3$, $Al(OH)_3$, $Ti(OH)_4$, etc. precipitated by NH_4OH filtered off, washed, ignited and weighed as Fe_2O_3, Al_2O_3, TiO_2, etc.; the CaO precipitated by $(NH_4)_2C_2O_4$ filtered off, washed, ignited and weighed as CaO; the MgO precipitated by Na_2HPO_4 filtered off, washed, ignited and weighed as $Mg_2P_2O_7$.

Process of Analysis.—Weigh 1 gram of the finely ground sample, transfer to a casserole covered with a clock glass, add 20 c.c. of 1:1 HCl, keeping the casserole well covered to prevent loss due to effervescence, and when the effervescence has ceased evaporate to dryness, taking care to prevent loss by spattering or too vigorous boiling. It is best to evaporate quietly on a steam plate with the cover off the casserole. If evaporation is accomplished by boiling, the cover must always be kept on. Finally, heat to 120°C. for one-half hour to render the silica insoluble. Cool the casserole and drench the contents with 20 c.c. of 1:1 HCl, and heat until everything has gone into solution except the silicic residue. Filter on an ashless filter, and wash well (about eight times) with hot dilute HCl, then several times with water. The filtrate will contain perhaps 1 per cent of the total silica. For exact work, evaporate the filtrate to dryness, dissolve the residue, filter and wash as above. Burn the two filter papers and their contents together in a platinum crucible, and ignite the silica over a blast for 15 minutes. If the siliceous matter is present in more than small amounts, and always if exact results are desired, it must be purified because of the presence of insoluble silicates. To accomplish this add eight times as much pure Na_2CO_3 as the weight of the siliceous residue, heat over a Meker burner until the mass has been fused at least 15 minutes, cool, dissolve in hot water, add 10 c.c. of 1:1 HCl, evaporate to dryness, bake, dissolve, filter and wash as before, adding the filtrate to the main one.

Carefully burn off the paper at a low temperature, ignite over a Meker burner or blast lamp for 15 minutes, cool and weigh.

For accurate results the SiO_2 must be purified. To the weighed platinum crucible and contents add a drop of sulfuric acid and 5 c.c. of HF and evaporate to dryness to expel the SiF_4. Ignite and weigh again. The loss in weight is SiO_2. When great accuracy is not required, and the silica is small in amount, one dehydration may be sufficient and the use of HF may be dispensed with.

After driving off the SiF_4 a small residue of oxides of iron, aluminium, titanium, and phosphorus may be left in the crucible. Transfer this residue to the filtrate from the silica by moistening with HCl, and rubbing with a policeman to loosen it, and then washing out of the crucible by means of a jet of water from the wash bottle.

To the filtrate, the volume of which should be about 100 c.c., carefully add NH_4OH with constant stirring until it just smells distinctly of NH_3. Should the precipitate be light colored and large in amount, indicating the probable precipitation of $Mg(OH)_2$, add 5 c.c. HCl and again NH_4OH as before. Now boil the liquid about three minutes, or until the odor of NH_3 is nearly gone. Remove from the heat, allow the precipitate to settle, filter quickly on an ashless filter and wash well with a hot 1 per cent solution of NH_4NO_3 until a test with $AgNO_3$ gives no indication of chlorine. Ignite and weigh the precipitate of Fe_2O_3, Al_2O_3,

P_2O_5, TiO_2 and SiO_2. If the precipitate of iron and aluminium hydroxides is large, it should be washed from the filter paper back into the beaker, dissolved in HCl, precipitated with ammonia, filtered and washed again. For strictly accurate results, two precipitations should always be made. The iron and titanium may be determined in the ignited precipitate after solution with H_2SO_4. For details see the "Analysis of Clays," page 378. The P_2O_5 is best determined in another sample, if desired. The sum of the oxides of iron, titanium, silicon and phosphorus when deducted from the total weight of the oxides gives the weight of the alumina.

Dilute the filtrate from the iron, aluminium hydroxide, etc. to about 200 c.c. If it is not distinctly alkaline add 5 to 10 drops of NH_4OH, heat to boiling and slowly add 80 c.c. of a solution of $(NH_4)_2C_2O_4$ also heated to boiling. Use a saturated solution of the salt diluted with an equal volume of water. Stir well during the addition of the reagent and for a minute or two afterward; then set aside until the precipitate of CaC_2O_4 has settled completely. Decant the liquid through a 9-cm. filter without disturbing the precipitate, wash the precipitate once by decantation, using about 50 c.c. of hot 1 per cent ammonium oxalate solution, then dissolve the precipitate in 10 c.c. of 1:1 HCl. Add 100 c.c. of water, heat to boiling, add NH_4OH slowly until just alkaline, then 5 c.c. more of $(NH_4)_2C_2O_4$ solution and heat for several minutes to enlarge the crystals. Let settle, filter, transfer the precipitate to the filter paper and wash six or seven times with hot 1 per cent ammonium oxalate solution. When the filtrate is to be concentrated for the determination of the magnesia, set aside the first filtrate and decanted liquid, and catch the subsequent washings in a separate beaker. Concentrate these by boiling down to a small volume and then add them to the first portion.

Instead of precipitating the lime as above, some chemists prefer to add 20 c.c. of a saturated $H_2C_2O_4$ solution, and then add NH_4OH to the hot solution very slowly and with stirring, until the solution is alkaline. This gives a coarse and easily filtered precipitate.

Dry the precipitate thoroughly, detach it as far as possible from the filter, put it in a weighed No. 0 porcelain crucible, burn the filter carefully on a platinum wire and add the ash to the contents of the crucible. Now drop concentrated H_2SO_4 onto the precipitate until it is well moistened, but avoid much excess. Heat the crucible (working under a "hood" to carry off the fumes), holding the burner in the hand and applying the flame cautiously until the swelling of the mass subsides, and the excess of H_2SO_4 has been driven off as white fumes. Finally, heat to a cherry red for five minutes. Do not use the blast lamp. Cool and weigh the $CaSO_4$. The weight of the $CaSO_4$ multiplied by 0.7350 gives the amount of $CaCO_3$ in the sample, or if multiplied by 0.4119 gives the amount of CaO.

Instead of changing the oxalate to sulfate, it is better to place the precipitate and filter paper in a platinum crucible, burn off the paper, cover the crucible with a lid and ignite at the high temperature of the blast lamp or a good Meker burner for 15 minutes, cool in a desiccator and weigh as CaO. This multiplied by 1.7847 gives the weight of the $CaCO_3$. The CaO should not stay in the desiccator more than an hour before weighing. The blast flame should be inclined, not vertical.

The filtrate from the CaC_2O_4 should be concentrated to 300 c.c. if over that volume; should any MgC_2O_4 separate, dissolve it by adding a little HCl. Heat to boiling and add 10 c.c. or a sufficient quantity of a saturated solution of Na_2HPO_4. Add NH_4OH until alkaline, then add 10 c.c. additional, then allow to cool with occasional vigorous stirring. The precipitate of $MgNH_4PO_4$ should be allowed to settle until the liquid is perfectly clear (about two hours). During this cooling and settling the solution should be stirred as much as possible, preferably continually by a mechanical stirrer. The successful precipitation of $MgNH_4PO_4$ is dependent upon much stirring. 10 c.c. of the phosphate solution is sufficient for about 20 per cent of $MgCO_3$; for dolomites more must be added.

Filter and wash with water containing one-tenth its volume of NH_4OH, sp. gr. 0.90 and a little NH_4NO_3. When there is a large amount of MgO present, the precipitate should be dissolved in a little HCl, made alkaline with NH_4OH and precipitated as before, using only 1 or 2 c.c. of phosphate solution. Dry the precipitate, detach it from the filter paper and burn the paper on a platinum wire; now ignite the precipitate and filter ash in a porcelain crucible, first heating carefully over a Bunsen burner till all volatile matter is driven off and it has been at a dull red-heat for some minutes, then finishing over the blast lamp for five or ten minutes. The ignited precipitate is $Mg_2P_2O_7$, the weight of which multiplied by 0.7572 gives the $MgCO_3$, or, by 0.3621, gives the MgO in the sample.

Notes on the Process.—Limestones generally contain silicates, some of which are soluble, some, like the feldspars, are not. The silicic acid liberated from the soluble silicates must be rendered insoluble by dehydration, thus, $H_2SiO_3 = H_2O + SiO_2$. This is accomplished by the baking. The presence of $CaCl_2$ renders the dehydration of the silicic acid easy at the temperature of the water bath. A much higher temperature is to be avoided as silica may recombine with the bases, especially MgO, and so either be redissolved on treatment with acid or render bases insoluble. One evaporation leaves perhaps 1 per cent of the silica soluble, and even after two evaporations semo silica will be found with the iron and alumina precipitate. The silica must be filtered off after each evaporation. With the silica thus filtered off are all the minerals insoluble in HCl. These are decomposed and the SiO_2 liberated by fusion with Na_2CO_3, followed by solution with HCl. See "Analysis of Clays," page 375.

The silica retains alkaline salts tenaciously. It must be washed thoroughly, first with hot water acidulated with HCl, then with cold water until the filtrate gives no test for chlorine when tested with $AgNO_3$.

The SiO_2 must be ignited to constant weight, as it retains water most tenaciously. A blast lamp is necessary to remove the last traces.

$Fe(OH)_3$ and $Al(OH)_3$ are insoluble in solutions of NH_4Cl, but a large excess of NH_4OH holds $Al(OH)_3$ in solution to a slight extent. This is separated by boiling off the excess of NH_4OH or by the presence of a large excess of NH_4Cl. Too much boiling renders the iron and alumina precipitates slimy and difficult to wash and filter. Hence, care is necessary in adding the NH_4OH to avoid large excess, so that a few minutes boiling will be sufficient.

The NH_4OH should be added slowly and with stirring, as a sudden addition will cause $Mg(OH)_2$ to precipitate with the $Fe(OH)_3$. The precipitate must be filtered promptly, as otherwise it will absorb salts which are washed out with difficulty. The precipitate should not be washed with pure water, as pure water causes this, like all colloidal precipitates, to disperse into such fine particles that they pass through the filter paper making the filtrate cloudy. The presence of an electrolyte is necessary to prevent this dispersion, hence a 2 per cent solution of NH_4NO_3 is, used, since the NH_4NO_3 entirely vaporizes upon ignition. Fluorides, if present, prevent the precipitation of $Al(OH)_3$ and sulfates also interfere.

$Mg(OH)_2$ is not completely soluble in NH_4OH unless NH_4Cl be present in considerable concentration. The NH_4Cl increases the solubility of $Mg(OH)_2$ through two effects: First, it decreases the concentration of OH ions from NH_4OH in accordance with the law of mass action; second, it forms with $MgCl_2$ a double magnesium ammonium chloride in which the magnesium does not ionize as magnesium ions strongly. $Mg(OH)_2$ separates as a white precipitate easily mistaken for alumina, so if the iron and aluminum hydroxide precipitate is large, it is best to redissolve it in considerable HCl and reprecipitate with NH_4OH. If much iron and alumina are present, the precipitate will certainly contain CaO and MgO, which must be removed by resolution and reprecipitation as above described. Solutions containing NH_4OH and CaO will absorb CO_2 on standing, precipitating $CaCO_3$; hence, the iron and aluminium hydroxides must be filtered and washed promptly. Distilled water often contains CO_2, which will cause a precipitation in the same way; hence, boiling the water before use is best. Cold water in a wash bottle rapidly absorbs CO_2 from the breath; such water should never be used in diluting the alkaline liquid holding the $Fe(OH)_3$ and $Al(OH)_3$ precipitate.

Calcium oxalate is very insoluble in the presence of $(NH_4)_2C_2O_4$, but is a difficult precipitate to filter and wash if not formed exactly right. On gentle ignition below visible redness it is changed to carbonate, and at still higher temperatures to CaO. The complete conversion to oxide requires a rather high temperature for a considerable time. However, the change is easily made complete and this method of determining the lime is quite accurate if care is taken to ignite to constant weight. The CaO formed is somewhat hygroscopic and should be weighed as soon as cooled in a desiccator. The action of concentrated H_2SO_4 on calcium oxalate converts it to $CaSO_4$. The action is not violent and the excess of H_2SO_4, provided it is moderate, can be driven off without danger of loss by spurting. Lumps in the crucible should be broken up before H_2SO_4 is added and care should be taken that the entire mass is moistened by H_2SO_4. $CaSO_4$ will stand the cherry-red heat of a Bunsen burner without alteration, but the higher heat of a blast lamp will cause it to lose SO_3.

It must not be forgotten that any strontium in the sample will precipitate with the calcium as strontium oxalate.

Calcium oxalate is somewhat soluble in hot water; hence, care should be taken not to use unnecessarily large amounts of hot water in washing it. At 95°C., 100 c.c. of water dissolves 0.0015 gram of CaC_2O_4, but the presence of $(NH_4)_2C_2O_4$ greatly decreases this solubility.

Magnesium will precipitate as oxalate in concentrated solutions; hence, when much is present the calcium oxalate should be dissolved and reprecipitated as described above. In the case of ordinary limestone, this is not necessary if the calcium is precipitated in properly diluted solutions, unless very accurate results are desired.

The composition of the magnesium phosphate precipitate is affected by the dissolved salts present and the condition of precipitation; hence, for accurate results a double precipitation must be made.

On concentrating the filtrate from the calcium oxalate, a crystalline precipitate of magnesium oxalate will sometimes separate. This can be redissolved in HCl and added to the solution. If it contains any calcium oxalate it will leave a milky solution which clears slowly.

As the liquid in which the magnesium is precipitated contains all the material added in the analysis, careless addition of reagents may give so strong a solution of ammonium and sodium salts that the precipitation of the magnesium phosphate will not take place promptly. However, the precipitation will be complete in time. To get rid of the ammonium salts, the filtrate may be evaporated to dryness with 3 c.c. of HNO_3, sp. gr. 1.42, for each gram of NH_4Cl, which will decompose and remove ammonium salts. Then any remaining magnesium may be precipitated.

There must be enough $(NH_4)_2C_2O_4$ solution added to convert all the magnesium as well as the calcium to oxalate, or calcium oxalate will not completely precipitate.

Sodium oxalate, being very sparingly soluble, will sometimes separate with the magnesium precipitate, especially when the solution is concentrated and much Na_2HPO_4 has been added; in this case, after partial washing, the precipitate must be dissolved in HCl and reprecipitated by NH_4OH.

Any manganese which was in the sample will precipitate chiefly with the magnesium. It can be determined very accurately in the ignited precipitate colorimetrically and the magnesium results corrected. Any barium in the sample will be found chiefly in the filtrate from the magnesium, but some will be with the calcium and some perhaps with the magnesium.

REFERENCES:

"Silica Separation," *J. Anal. App. Chem.*, **4**, 159.

"Magnesium Calcium Separation, Fresenius, Quantitative Analysis," Pars. 73, 74, 101, 104, 154.

For refined methods of limestone analysis, see U. S. Geological Survey *Bull.* 422, "The Analysis of Silicate and Carbonate Rocks," by W. F. HILDEBRAND.

Instead of determining the total silica as is given in the above process, it is the custom in many places to determine what is called the "insoluble siliceous matter." This is done by dissolving the sample in strong HCl, evaporating to dryness to dehydrate any soluble silica and then filtering off, washing and weighing the residue. Iron and alumina, lime and magnesia are then determined in the filtrate as in the filtrate from the silica. The insoluble siliceous matter, however, generally is not all silica. Since it is just about as quick to ignite and determine silica accurately, the determination of "insoluble siliceous matter" seems hardly worth while.

THE DETERMINATION OF CO_2 IN LIMESTONE

This determination is generally not necessary for technical purposes, but it may very easily be done by use of the apparatus shown in Fig. 3. An 0.5-gram sample is placed in the flask, covered with 100 c.c. of water, and 10 c.c. of H_2SO_4 added slowly so that not more than three or four bubbles per second pass through the KOH bulb. When effervescence ceases, the acid in the flask is heated to boiling, and then a liter of air is drawn through the apparatus. The increase in weight in the KOH bulb gives the amount of CO_2. The KOH bulbs must, of course, show no increase or decrease in weight when a liter of air is aspirated through as a blank before the regular determination.

Sometimes it is necessary to determine carbonaceous material like organic matter in minerals or rocks, such as clays, shales, etc. This is carried out exactly as directed above for CO_2, except that, instead of using dilute H_2SO_4, strong H_2SO_4 and chromic acid are used. Transfer the carefully weighed sample to the flask, add 20 c.c. of water, dissolve 4 grams of chromic acid in 4 c.c. of water and pour it into the flask through the funnel tube, following it with 2 or 3 c.c. of water to wash out the tube. Now put into the bulb of the funnel a quantity of concentrated H_2SO_4, equal to about two and a half or three times the volume of the liquid in the flask.

This volume can be estimated by pouring water into a second similar flask until it appears to contain the same amount of liquid as the first and then measuring the quantity used.

The acid used should be purified from any trace of organic matter which it may contain, by adding a little chromic acid to a quantity of it and then heating it to about 200°C. for a few minutes. Let it stand till cool before using.

Now open the stop-cock and run the acid slowly into the flask, being careful to avoid too violent action. When the acid is all in, shake the flask carefully to mix the contents.

The evolution of CO_2 will begin at once. Finally heat carefully to boiling, so regulating the heat that the evolution of the gas does not take place too rapidly. The gas should not pass through the potash bulbs faster than two or three bubbles per second. The boiling should be continued two or three minutes. At the end of this time but little gas should be coming over through the bottles; but, as some oxygen is likely to be given off by the chromic acid mixture, it is usually not possible to continue boiling till the evolution of gas ceases. Now withdraw the lamp and immediately open the stop-cock of the funnel tube to admit air and prevent back suction. Connect the funnel tube with the soda-lime guard tube, and let the apparatus cool a few minutes. Then aspirate carefully until a volume of air has been drawn through equal to seven or eight times the capacity of the apparatus.

Detach the absorption apparatus and weigh it. The total gain in weight will be the amount of CO_2 formed, and this multiplied by 0.2727 gives the amount of carbon in the sample taken.

The greatest care and "handiness" are necessary, but, with skill, duplicates should agree within 0.01 per cent.

The solution should not be brought to the boiling point too rapidly. By raising the temperature slowly, time is given for the reaction and most of the carbon will be oxidized before the liquid begins to boil. If much unoxidized carbon is present in the boiling liquid, particles of it are likely to be carried up onto the sides of the flask, where they will adhere and so escape oxidation.

If white fumes form toward the end of the boiling, let the flask cool until they disappear before aspirating.

The foregoing method of determining carbon by combustion with chromic acid is very accurate if conducted carefully. It has the advantage of demanding no special or expensive apparatus.

Arrangement of the Apparatus.—Figure 3 shows a convenient form of train for the use of students. It is compact, needs no special clamps and can be taken apart and set away in a laboratory desk. *C* is an Erlenmeyer flask of about 250-c.c. capacity, fitted with a two-hole rubber stopper; into one hole is inserted a bulb funnel tube *B*, having a glass stop-cock, and into the other a delivery tube *M* for the gas.

This latter should be of rather large diameter and so inclined that everything condensing in it will run back into the flask. It is a good plan to have it cooled by a "water jacket" *D*, consisting of a larger tube surrounding the smaller, the space between the two being filled with water.

A small guard tube *A*, filled with "soda lime" is fitted to the top of the funnel tube.

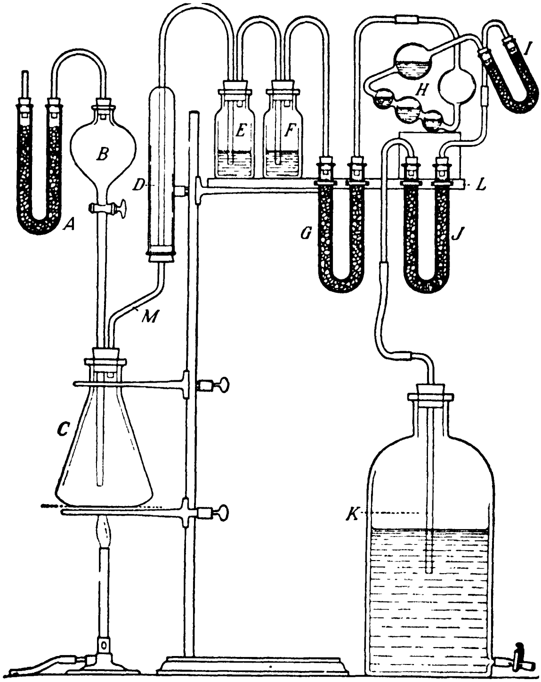

Fig. 3.

This serves to remove any CO_2 from the air drawn into the flask. It must be so arranged as to be easily connected and disconnected.

The delivery tube is connected with the purifying and absorbing apparatus (or "train") arranged in the order shown.

E is a bottle of 50- to 75-c.c. capacity, containing about 30 c.c. of a solution of silver arsenite in dilute sulfuric acid.

This serves to absorb any chlorine, HCl or CrO_2Cl_2 in the gas. A solution of silver sulfate may be used instead, but this does not absorb chlorine nor chromyl chloride and is usually preceded by a bottle containing pyrogallic acid dissolved in a solution of potassium oxalate (LANGLEY). When using the arsenite, this is unnecessary, as it is oxidized to arsenate by the chlorine and the silver precipitated as chloride.

The arsenite solution is prepared as follows: Dissolve 2 grams of pulverized As_2O_3 in the smallest possible quantity of a dilute solution of KOH. Dilute to 250 c.c. and add dilute H_2SO_4 till the solution is neutral to litmus paper. Now add a solution of $AgNO_3$ as long as a yellow precipitate forms, carefully keeping the solution neutral by adding a solution of KOH drop by drop as needed. Stir the liquid till the precipitate clots, let it settle and wash it thoroughly by decantation. Finally, dissolve the precipitate in a slight excess of dilute H_2SO_4 (10 per cent). Dilute to about 150 c.c. and filter from any undissolved AgCl. The solution keeps well.

The silver sulfate is made by dissolving about 0.5 gram of $AgNO_3$ in a little water, adding 1 c.c. concentrated H_2SO_4, evaporating till the HNO_3 is all expelled, cooling and diluting largely with water. Ag_2SO_4 is only sparingly soluble.

F is a bottle containing 20 or 30 c.c of pure concentrated H_2SO_4.

This takes out all the water vapor from the gas.

G is a U-tube containing granular $CaCl_2$. Fill about an inch of the tube, on the side next to the H_2SO_4 with cotton and moisten the top of this with a drop of water (BLAIR). It is shown with its connecting tube in Fig. 4, *C*.

The object of this $CaCl_2$ is to absorb water and to bring the gas stream entering the absorption apparatus (*H* and *I*) into the same condition, as to moisture, in which it leaves it. H_2SO_4 will dry air more completely than $CaCl_2$, hence, if the gas entered through H_2SO_4 and left through $CaCl_2$ it would carry out more moisture from the KOH bulbs than it brought in, and so result in loss of weight. It also serves to catch any white fumes of H_2SO_4 carried over by the gas.

Dried $CaCl_2$ and not the fused salt should be used. This latter is usually alkaline from free CaO and will absorb some CO_2.

H (Fig. 3) shows the Liebig's potash bulbs. These contain a clear solution of KOH of about sp. gr. 1.27 (about 30 per cent).

This solution absorbs the CO_2, but not *completely* unless the gas stream is slow. The solution gives up a little water to the gas passing through. If made stronger than directed it deposits K_2CO_3, which may clog up the tube.

As caustic potash frequently contains nitrites and almost invariably traces of $Fe(OH)_2$, a fresh solution will absorb oxygen, the $Fe(OH)_2$ gradually precipitating as $Fe(OH)_3$. If the potash bulbs are filled with such a solution they will frequently continue to increase in weight for some time if air alone is aspirated through them. This troublesome difficulty may be entirely overcome if the potash solution is heated to boiling before using and a solution of potassium permanganate added drop by drop until a faint persistent green tint is produced. The liquid is then allowed to cool and settle, and the clear solution decanted for use.

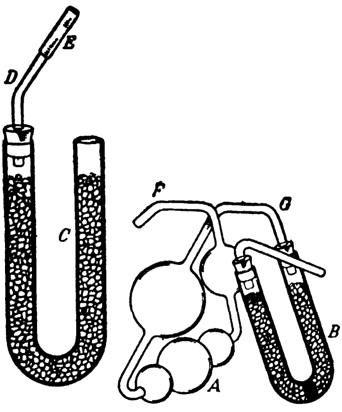

Fig. 4.

I is a small U-tube, with the limb next the potash bulbs filled with granular soda lime. This should not be too dry. The other limb is filled with granular $CaCl_2$.

This tube serves to catch the trace of CO_2 escaping the bulbs, and also to retain the moisture carried over from the potash bulbs. Soda lime is a more rapid and complete absorbent for CO_2 than the KOH in the bulbs, but it is soon exhausted. By letting the bulbs do most of the work and using only the soda lime as a guard, it lasts for many operations and retains every trace of the CO_2. The potash bulbs and the soda lime—calcium chloride—tube are the parts of the train to be *weighed.* They may be weighed separately or together. In the latter case they should be permanently combined into one piece as shown in Fig. 4, *A* and *B*, a very convenient arrangement. The ends of the tubes are bent over, as shown at *F* and *G* (Fig. 4). When connected up, the tube and bulbs should so support each other as to stand upright safely.

J is a U-tube similar to the last, but larger, having the limb next to *I* filled with $CaCl_2$, and the other with granular soda lime.

This serves as a guard tube to prevent moisture or CO_2 working back into the absorption apparatus from the aspirator. It can be used almost indefinitely without becoming exhausted.

K is an aspirator for sucking air slowly through the apparatus. This must be arranged so that it can be easily attached and detached. It can be made from a 5-pint acid bottle by boring a hole near the bottom with a pointed file dipped in turpentine, fitting a glass tube in this by a rubber ring and then attaching to this a rubber tube and pinch-cock.

Notes on the Above Apparatus.—It is essential that none of the chromic acid solution come into contact with the rubber stopper or connections, as it would, of course, form CO_2. For similar reasons it is necessary that the glass stop-cock in the funnel tube be free from grease of any sort.

A flask provided with a ground-glass cap, into which the tubes are fused, may be substituted for the rubber-stoppered flask as described.

Liquids always absorb some CO_2, hence the volume of all absorbing liquids used in the purifying train must be small. The CO_2 absorbed is, however, given up again to a current of air passed through them for some time.

This apparatus is very convenient for determining both the CO_2 and total carbon in clays and limestones. When CO_2 only is wanted, the chromic acid is omitted.

THE VOLUMETRIC DETERMINATION OF LIME

Instead of weighing the calcium as $CaSO_4$ or CaO, it may be determined by measuring the volume of a standard solution of $KMnO_4$ required to oxidize the oxalic acid which it contains. The precipitate is first dissolved in dilute sulfuric acid, the liberated oxalic acid is then titrated by $KMnO_4$. The reactions may be summed up as follows:

$$5CaC_2O_4 + 8H_2SO_4 + 2KMnO_4 = 5CaSO_4 + K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

This reaction takes place rapidly at 70°C. The first few drops of permanganate color the liquid and a few seconds will elapse before color disappears, then the reagent may be added rapidly. This delay in starting is entirely removed if a few drops of a strong solution of $MnSO_4$ are added to the liquid before titration. As the titration proceeds, rapid effervescence of CO_2 takes place, resulting in a spraying out of some of the liquid unless the titration is done in a flask.

Solution Required.—The solution required is a standard solution of potassium permanganate. The same solution can be used as for the determination of iron in ores. The iron value multiplied by 0.8960 gives the $CaCO_3$ equal to 1 c.c. of permanganate in the above reaction; however, it is best to standardize the permanganate against pure Iceland spar or pure lime, which is dissolved in HCl, and the calcium precipitated as oxalate as in the above process.

Process.—For limestone low in magnesia:

Weigh out 89.6 times the iron value of the permanganate, if it is desired to report as carbonate, or 50.2, if it is desired to report as CaO. The sample should be finely ground. Transfer to a small platinum crucible, and ignite cautiously to destroy organic matter. Transfer the ignited powder to a 400-c.c. beaker, add 20 c.c. of water, cover and then add 15 c.c. of HCl, sp. gr. 1.19, and 3 or 4 drops of HNO_3. Boil until all the soluble matter is dissolved and all the CO_2 expelled. Wash off and remove the cover and dilute the liquid to about 150 c.c. with water free from CO_2. Add NH_4OH in slight excess, and heat to boiling. Then, without filtering off the precipitated iron and aluminium hydroxides, precipitate the CaC_2O_4 exactly as in the gravimetric analysis. Continue the stirring two or three minutes after the addition of the hot ammonium oxalate solution and then let settle until nearly clear, which should require not over five minutes if the work is correctly done.

Decant through a 9-cm. filter, pouring off very closely. The precipitate should be so dense as to render this easy. Add 30 c.c. of hot water to the precipitate, stir well, let stand three or four minutes, and again decant. Repeat the decantation a third time and then transfer the precipitate to the filter and wash about eight times with hot water.

Reserve the filtrate and washings for the determination of magnesia.

Now run 10 c.c. of water through the filter and catch it in a small beaker, add ½ c.c. sulfuric acid, heat to 70° and add a drop of standard permanganate solution. If the color is not discharged in two or three minutes, the precipitate is sufficiently washed; otherwise continue the washing and test again. Then wash the CaC_2O_4 back into the beaker in which it was precipitated, add water, if necessary, to make a volume of at least 150 c.c., place the beaker under the funnel and run through the filter into the beaker 30 c.c. of 1:3 H_2SO_4. Stir the contents of the beaker thoroughly while the acid runs in, to avoid the separation of $CaSO_4$. Now wash the funnel and filter thoroughly with hot water. Dilute the liquid in the beaker to 350 c.c., heat to 70°C. and titrate with permanganate to a faint pink color not disappearing in two or three minutes.

To test the filter paper for undissolved CaC_2O_4, it may be added to the contents of the beaker and stirred up in it; if the washing has been careful, it will not cause the discharge of the color.

If the factor weight was used, the number of cubic centimeters of the permanganate required for the titration will equal the percentage of $CaCO_3$ or CaO in the sample, for if 1 c.c. equals 0.01 gram Fe, it will equal 0.00896 gram $CaCO_3$ or 0.00502 gram CaO, and if 100 c.c. were used it would be equal to 0.896 gram $CaCO_3$ or 0.502 gram CaO, which were the samples to be taken.

The CaC_2O_4 obtained in the first method given, instead of being weighed as $CaSO_4$ or CaO, may be dissolved and titrated by permanganate as in the volumetric process.

When magnesium is present in considerable amount, two precipitations of the CaC_2O_4 must be made, for the same reason that two precipitations are required in the gravimetric process when magnesia is high, *i.e.*, because the CaC_2O_4 will carry down with it some MgC_2O_4. If two precipitations are to be made it is necessary to filter off the $Fe(OH)_3$ separately, as it will be reduced by the oxalic acid when the CaC_2O_4 is dissolved in HCl and interfere with the magnesia determination

Notes on the Process.—Ignition of the sample is necessary to destroy any organic matter present, which if not destroyed, will reduce $KMnO_4$ and cause the calcium results to run high.

Unless the precipitate of CaC_2O_4 is stirred up in a considerable volume of water, when the first few cubic centimeters of sulfuric acid are added to dissolve it a dense flaky precipitate of $CaSO_4$ may separate, which is likely to occlude solution and obscure the end point.

If the $KMnO_4$ is added too rapidly during the titration or the solution is not well stirred, brown MnO_2 may separate out; if this is not redissolved, the results will be inaccurate.

All water used in diluting the solutions in this process for lime must be free from CO_2 or $CaCO_3$ will come down with the CaC_2O_4, and, as this does not react with the permanganate, the lime will run low. For the same reason it is important that all CO_2 be expelled from the solution of the sample in HCl by boiling it thoroughly.

REFERENCES ON VOLUMETRIC DETERMINATION OF LIME AND MAGNESIA:
FRESNIUS, "Quantitative Analysis."
SUTTON, "Volumetric Analysis."
HANDY, *J. Am. Chem. Soc.* (1900), 31.
MEADE, *J. Am. Chem. Soc.* (1899), 746.
ULKE, *Eng. Mining J.*, **69** (1900), 164.
KONNICK, *J. Soc. Chem. Ind.* (1900), 564.
For the Conditions for the titration of oxalate by permanganate, see McBRIDE, *J. Am. Chem. Soc.* (1912), 393.

THE DETERMINATION OF FREE LIME

This is based on the fact that uncombined CaO forms soluble compounds with sugar in solution in water and that calcium carbonate, alumina, ferric oxide, magnesium carbonate and free magnesia do not dissolve. The writer has carefully tested the effect of the presence of free magnesia upon this determination of free lime and finds that it is without influence.

The method is very convenient for the determination of free lime in burnt and hydrated limes.

Process of Analysis.—Place 1 gram of the finely ground sample in a 200-c.c. flask, add 15 grams of cane sugar and 50 c.c. of water and shake the flask vigorously for several minutes. Dilute to the mark, mix the solution thoroughly and let the residue settle until the solution is clear, pipette off 100 c.c. and titrate the lime with standard HCl, using phenolphthalein as indicator. If the HCl is N/5, each cubic centimeter is equal to 0.005607 gram of CaO. Phenolphthalein is prepared as directed on page 62.

To prepare the N/5 hydrochloric acid, proceed as follows: Dilute 17.0 c.c. of HCl, sp. gr. 1.19, to 1 liter and standardize exactly as directed on page 61 for the standardization of HNO_3, except that 0.53 gram Na_2CO_3 should be weighed; or ignite 2.002 grams of pure, dry, powdered Iceland spar ($CaCO_3$) in a platinum crucible over a Meker burner until constant weight is attained, dissolve completely in sugar solution as directed above, dilute to 200 c.c., pipette off 50 c.c. and titrate with the acid to be standardized. If the acid is exactly N/5, 50 c.c. will be required. If the acid is too strong, as it will likely be, dilute the calculated amount and titrate again.

Note.—Hydrochloric acid makes the best standard acid for general use because it forms readily soluble salts with all the radicals commonly titrated with acids, is easily obtained pure, the strength of the acid is easily verified by means of silver nitrate, the dilute solutions used suffer no appreciable loss when boiled and the strength of the acid does not change on keeping.

Some chemists prefer phenol instead of sugar to dissolve the lime.

The determinations of sulfur and phosphorous in limestone are carried out as directed for iron ores.

References:

Stone and Schenk, *J. Am. Chem. Soc.*, **16,** 721.
Weisberg, *Chem. News*, **82,** 284.
Mellor, "Quantitative Analysis," p. 527.

A Method for the Titration of Calcium Oxide or Hydroxide in the Presence of Aluminates or Silicates.—By the method here given, CaO or $Ca(OH)_2$ can be determined without difficulty in the presence of $CaOSiO_2$, $2CaOSiO_2$, $CaOAl_2O_3$, $5CaO3Al_2O_3$, $CaCO_3$ or $CaSO_4$. If $3CaOSiO_2$ is present, the method is still applicable but the end point is a little harder to recognize; to a less extent the same is true if MgO is present. With $3CaOAl_2O_3$, special precautions must be taken to insure the absence of H_2O. The alcohol is redistilled from the quicklime immediately before using. The method follows: In a 250-c.c. flask, put 2 c.c. of glycerol and 10 c.c. of alcohol, add the finely powdered sample in sufficient quantity to give about 0.1 gram of free CaO, add 5 drops of phenol solution, bring to a boil and keep near the boiling point throughout the titration. Titrate with 0.2 N alcohol solution of $NH_4C_2H_3O_2$. The end point is reached when the pink color is discharged and does not return after boiling for one minute.

Reference:

Emley, *Trans.* Am. Ceram. Soc., **17,** 740.

CHAPTER III

THE DETERMINATION OF IRON IN ORES

The iron of iron ores is present chiefly as the minerals hematite (Fe_2O_3), limonite ($2F_2O_3.3H_2O$) magnetite (Fe_3O_4), siderite ($FeCO_3$), ilmenite ($FeTiO_3$) and other oxidized compounds. A small amount may be present as pyrite (FeS_2), and in silicates such as biotite, enstatite and pyroxene. All these minerals are soluble in HCl except ilmenite and the silicates.

Many iron ores give up practically all of their iron to hydrochloric acid, provided that the acid be strong and the ore be very finely pulverized. On the other hand, many ores contain a small amount of iron in such a state of combination that it will not dissolve in hydrochloric acid. In such cases the residue left after treatment with acid must be fused and the iron determined in the fusion.

If the residue after treatment with HCl is pure white with no dark specks, the iron is probably all dissolved unless the ore contains TiO_2, in which case an insoluble compound of iron, titanium and phosphorus may remain which will not color the residue.

Sometimes previous ignition of the ore will cause the ore to dissolve more completely in acid.

All methods for the determination of iron in ores depend upon reducing the iron in acid solution to the divalent form, then measuring the amount of a standard oxidizing agent required to oxidize the iron back to the trivalent condition. The reducing agents are metallic zinc, metallic aluminium, $SnCl_2$, H_2S, SO_2. The oxidizing agents are $K_2Cr_2O_7$ and $KMnO_4$.

THE DETERMINATION OF IRON BY POTASSIUM DICHROMATE AFTER REDUCTION OF THE FERRIC CHLORIDE BY STANNOUS CHLORIDE

The process depends upon the following reactions:

A strongly acid solution of $FeCl_3$, if boiling hot, is almost instantly reduced to $FeCl_2$ by a solution of $SnCl_2$, the end of the reaction being shown by the disappearance of the yellow color of the ferric ion.

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4.$$

Any slight excess of stannous chloride can be removed by adding $HgCl_2$, forming a white precipitate of HgCl, which is without action on iron salts or dichromate, the stannous chloride being oxidized to stannic chloride by the $HgCl_2$.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$

The reaction is not instantaneous, and after the addition of the $HgCl_2$ at least two or three minutes should elapse before titration. The reaction is satisfactory, provided not too much $SnCl_2$ is present and the $HgCl_2$ is in large excess and added all at once. Otherwise, metallic mercury may be formed as a gray precipitate which will act on the dichromate and cause false results. Thus, $SnCl_2 + HgCl_2 = SnCl_4 + Hg$. This reaction is at once detected by the gray color of the precipitate and entirely vitiates the results. If the solution is very hot, the difficulty of avoiding reduction to mercury is increased.

When a solution of potassium dichromate is added to a solution of $FeCl_2$ containing a considerable excess of HCl, the $FeCl_2$ is immediately oxidized to $FeCl_3$ with a corresponding reduction of dichromate to $CrCl_3$, giving a green color to the solution. The reaction is

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

In the absence of an excess of HCl the solution becomes yellowish instead of green, and more HCl must be added, otherwise error will be made.

The end point, that is, the completion of the oxidation, is determined by the use of potassium ferricyanide. When a drop of the solution containing a ferrous salt is added to a drop of a dilute solution of ferricyanide an intense blue color is produced, while solutions containing only ferric salts give a yellow-brown color with ferricyanide. The ferricyanide solution must be fresh, as it is reduced on exposure to light or on standing, with a formation of ferrocyanide, and, of course, the salt must be pure; some ferricyanide is contaminated with ferrocyanide, which gives a blue color with both ferric and ferrous iron and, consequently, cannot be used. Zinc cannot be used as a reducing agent in the dichromate method because it forms the insoluble $Zn_3(Fe(CN)_6)_2$ with the ferricyanide, unless the electrometric method is used.

Preparation of the Solutions. 1. Potassium Dichromate Solution.—Place a platinum crucible containing a sufficient quantity of dichromate in a sand-bath with the sand as high on the outside as the dichromate on the inside of the crucible. Heat until fusion of the dichromate just commences around the sides of the crucible. Then remove the crucible.

Weigh out exactly 8.779 grams of the cold powdered dichromate; dissolve in 300 c.c. of cold water, transfer to a liter flask, dilute to 1 liter and shake well to insure thorough mixing. Of this solution 1 c.c. should oxidize exactly 0.01 gram of iron from ferrous to ferric condition.

Now to test the solution, dissolve 2.81 grams of pure ferrous ammonium sulfate, $(NH_4)_2Fe(SO_4)_2 6H_2O$, in 75 c.c. of water containing 7 c.c. of HCl. The salt contains 14.24 per cent Fe and should require just 40 c.c. of the dichromate solution to titrate it. Run in from a burette 39 c.c. of the dichromate solution, stir well and add a drop of the solution to a drop of the ferricyanide solution placed on a white porcelain plate. A blue color forms if ferrous iron is present. Now add the dichromate solution drop by drop, testing the liquid after each addition until on testing with ferricyanide a yellow color is produced instead of a blue after one-half minute. If the burette is properly calibrated and the dichromate properly made, the liquid in the burette should now read 40 c.c. If it does not, repeat the test and make a factor of correction. For example: If, instead of 40 c.c. of dichromate, 40.2 were required, the strength of the dichromate in terms of iron would be $\frac{40}{40.2} \times 0.01 = 0.0099502$ gram per cubic centimeter. For volume corrections see Table 7, page 436. The solution keeps indefinitely.

The object of the heating of the dichromate is to expel water and destroy any trace of organic matter present.

If the salt is strictly pure and the fusion has been carefully conducted it will dissolve to a perfectly clear liquid which will check exactly with the iron salt if this is also pure. This makes a double check on the solution and the results obtained by the two methods should closely agree. Of course, the burette used must be carefully calibrated.

The dichromate should also be checked against a U. S. Bureau of Standards standard ore and against purest iron wire, as directed on page 38.

Some of the dichromate on the market contains excess of chromic acid, and gives too strong a solution. When this is true, the salt should be purified by recrystallization. If the salt is heated too hot, especially if it is not pure, the solution will be turbid. If more than a trace of this turbidity shows, a new solution should be prepared.

2. **Stannous Chloride Solution.**—Dissolve stannous chloride in four times its weight of a mixture of three parts of water and one of HCl, sp. gr. 1.2. Add scraps of metallic tin and boil until the solution is clear. Keep this solution in a closed dropping bottle containing metallic tin.

3. **Saturated Solution of Mercuric Chloride.**—Keep an excess of salt in a bottle and fill it up with water from time to time.

4. **A Very Dilute Solution of Potassium Ferricyanide.**—Dissolve a piece half as big as a small pea in 50 c.c. of water. This solution must be made fresh when wanted, as it does not keep.

The ferrous ammonium sulfate used for standardization as directed above is not satisfactory for exact work, owing to its tendency to change in composition through oxidation and loss of moisture. It is necessary to check the results obtained by this reagent against other standard materials. The most satisfactory are the U. S. Bureau of Standards standard iron ore and purest iron wire as supplied by reputable chemical supply houses. To standardize against iron ore, proceed exactly according to the directions for the analysis of iron ores, except that the ore must be dried at 105°C. To standardize the $K_2Cr_2O_7$ against pure iron wire, proceed as follows:

Carefully clean the iron wire by rubbing with fine emery cloth and clean filter paper, then weigh carefully 0.3000 to 0.4500 grams of the wire, cut in short lengths. Put the wire in a 200-c.c. flask and dissolve in 15 c.c. of $1:2HNO_3$. When dissolved add 5 c.c. of strong HCl and 3 c.c. of strong H_2SO_4, evaporate until the H_2SO_4 gives off dense white fumes. This insures the destruction of all carbonaceous material in the iron which might affect the standardization and expels all HNO_3. Cool, add 10 c.c. of strong HCl and 100 c.c. of water, heat to boiling and drop in $SnCl_2$ solution drop by drop until the yellow color of the ferric chloride just disappears. Then add 2 drops more. Cool, add 15 c.c. of $HgCl_2$ solution, stir for two minutes and titrate until test with $K_3Fe_2(CN)_6$ solution on a white plate shows the titration to be complete. Care should be taken that the smallest amount possible of the solution which is being titrated is removed for testing. Correct for the impurities in the wire, which is usually about 99.8 per cent pure.

The other solutions keep indefinitely. The $SnCl_2$ solution, however, absorbs oxygen from the air and hence must be kept closed. Should it grow turbid or deposit a white precipitate, add more HCl and metallic tin and heat until clear.

Process for the Analysis.—Pulverize the ore in an agate mortar until it is so fine that no grit can be felt between the teeth. It is best to grind a small amount at a time.

Weigh out 1 gram; put it into a small dry beaker, brushing off the watch-glass carefully. Add 25 c.c. of HCl, sp. gr. 1.2, cover the beaker with a watch-glass and set it on a hot plate. Digest at a temperature just short of boiling until all iron is dissolved and on shaking the beaker the residue appears light and flotant, and free from dark heavy particles. This may take from fifteen minutes to an hour or more, according to the nature of the ore. Dilute the solution to two or three times its original volume, filter through a small filter into a 250-c.c. beaker, and wash the residue on the filter until it is free from acid. Heat the solution to boiling, drop in the tin solution slowly until the last drop makes the solution colorless, indicating complete reduction; then add 2 drops additional. If too much stannous chloride is dropped in by mistake, add permanganate to the solution until a yellow color appears, then again add stannous chloride drop by drop until the yellow just disappears. Dilute with cold water to 200 c.c., then add all at once, with vigorous stirring, 15 c.c. of the mercuric chloride solution. Let stand three or four minutes. A slight white precipitate should form. If none, or a heavy grayish precipitate, forms, the result is rendered doubtful and the determination should be repeated.

Divide the solution into halves approximately. Into one-half run the standard dichromate solution until the end point is roughly obtained, then add the other half, washing the solution out of the beaker thoroughly, and complete the titration accurately. The final end point is known approximately from the end point obtained on the first half of the solution. In this way it is not necessary to consume much time approaching the end point. The number of cubic centimeters used multiplied by the iron factor of the dichromate and then by 100 gives the percentage of iron in the sample.

If by any accident too much of the dichromate solution is run in, add 1 c.c. of a dilute solution of ferrous sulfate, finish the titration and read the burette. Then add 1 c.c. more of the same solution, again finish the titration and read the burette. Deduct the difference between the first and second readings from the first reading to find the true end point.

Notes on the Process.—When an ore is with difficulty decomposed by HCl, the addition of 2 or 3 c.c. of $SnCl_2$ solution to the ore and acid in the beaker will greatly accelerate the solution of the ore. In this case, after the color and nature of the residue show complete extraction, carefully add a solution of $KMnO_4$ to the contents of the beaker until the yellow color of ferric chloride again appears, then dilute and proceed as usual. The object of the permanganate is to oxidize the excess of stannous chloride.

In the case of unknown ores, or of an ore in which not all of the iron can be completely dissolved by HCl, the residue after solution in HCl must be fused to render soluble the rest of the iron. Place the filter in a platinum crucible, burn off the paper, add 2 or 3 grams of Na_2CO_3 and fuse over a Meker burner until all minerals are decomposed. Dissolve the fusion in 50 c.c. of water and 5 c.c. of HCl, heat to boiling, add a drop of stannous chloride solution and then place a drop of the solution on a white plate and test for ferric iron with KCNS. If a red color is produced, more stannous chloride is needed, but the chances are that not more than one drop of stannous chloride will be required. The reason for using KCNS is that after fusion in platinum some plantinum always goes into solution, and stannous chloride produces with this a yellow color, so that the end of the reduction cannot be told by the disappearance of the yellow color of ferric chloride.

Now add $HgCl_2$ and titrate as in the case of the main solution.

There is danger of loss of iron if a concentrated solution of $FeCl_3$ in HCl is boiled; hence too great concentration of the solution and too hard boiling must be avoided.

In testing the solution to see if the end point is near, care should be used that only very small drops of the solution which is being titrated are removed, otherwise an appreciable amount of untitrated iron may be taken out, causing low results. As the end point is approached the blue color obtained when the test is made with ferricyanide grows less intense until the addition of one more drop of dichromate to the iron solution gives a test with no trace of green color.

In the case of mill cinder and other decomposable slags, add 20 c.c. of water to the finely powdered material, and stir up well to prevent the cinder caking on the bottom of the beaker; then add 25 c.c. HCl and proceed as before.

Titanium will not affect this process, provided care be taken to fuse the residue and add the solution of the fusion to the main solution. When zinc is used to reduce the iron, titanium is also partly reduced.

The presence of vanadium will vitiate the results, as it is reduced by $SnCl_2$ and oxidized by dichromate.

The porcelain plate upon which the tests for the end point are made should be prepared by warming a plate on a steam-bath, then rubbing with a piece of paraffin so as to cover the whole plate with a thin skin of paraffin. The test drops will not then spread over the plate.

For the electrometric method see page 252.

THE DETERMINATION OF IRON BY TITRATION BY POTASSIUM PERMANGANATE AFTER REDUCTION BY METALLIC ZINC

This is a widely used process. The time of the actual titration is shorter than with the dichromate, as an outside indicator is unnecessary because the permanganate acts as its own indicator. The least bit of permanganate added to the solution in excess of that required to titrate it gives to the solution a permanent pink color.

On the other hand, the permanganate is much more liable to change than the dichromate and is also much more subject to reduction by other materials, as, for example, organic matter in the ore or solution.

Titration by permanganate in HCl solution is only permissible under certain closely regulated conditions. The amount of HCl must be small and a certain amount of manganese salt must be present, otherwise the HCl will cause some reduction of the permanganate, giving a brown color to the solution and making the results run too high. The presence of phosphoric acid is desirable, as it changes the yellow ferric chloride to colorless ferric phosphate, thus making the end point plainer. The phosphoric acid is also said to prevent the reduction of permanganate by the HCl.

Reduction of the iron by zinc is accomplished either by adding granulated zinc to the solution in an Erlenmeyer flask and boiling a few minutes or by using the "reductor" introduced by Clemens Jones, in which the iron solution is filtered through a column of amalgamated granulated zinc.

Zinc is such a powerful reducing agent that many substances are reduced by it to oxidizable forms which vitiate the result. Thus the iron solution must not contain arsenic, titanium, vanadium or nitrates, since lower oxides are formed which are oxidized by permanganate. Nitrates are reduced ultimately to ammonia, which does no harm, but frequently the reduction is only partial, resulting in the formation of hydroxylamine (NH_2OH), which is oxidized by permanganate. The writer has known of results for iron running as high as 125 per cent because the H_2SO_4 used had in it HNO_3 which was reduced to NH_2OH.

As the zinc is never pure, a blank must be run on it and the amount obtained subtracted from the permanganate used in the regular titration. If pure zinc is used without being amalgamated with mercury, the zinc used must be completely dissolved each time, as it reduces some iron on it as metallic iron, making the result run low. When the zinc is amalgamated the reduction is much less powerful; in fact, if the mercury coating is too heavy the reduction of the iron is apt to be too slow. There should be not more than 5 per cent free acid present.

The reactions involved are: $Zn + Fe_2(SO_4)_3 = ZnSO_4 + 2FeSO_4$. $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$.

Solution Required. Permanganate Solution.—A convenient solution is one in which 1 c.c. equals 0.01 gram of iron, *i.e.*, one which has in 1 c.c. sufficient permanganate to oxidize 0.010 gram of iron from divalent to trivalent condition. This will contain 5.659 grams of $KMnO_4$ to the liter.

To prepare the solution, dissolve 5.7 grams of pure permanganate of potassium in water, and, when dissolved, dilute to 1 liter. The solution should stand a day or so before being standardized. It is likely to alter rapidly at first, but in time reaches a comparatively stable condition if protected from light and dust. Where large quantities are used it is a good plan to make up a carboy ahead and let it be "ageing." The container should be painted black to keep out light.

Standardization of the Permanganate.—The reducing reagents used as standards are: Pure iron wire, ferrous ammonium sulfate, sodium oxalate and oxide of iron or iron ore in which the iron content is known. It is best to standardize against several of these reagents and the results should agree closely. If they do not, purer materials should be obtained.

To standardize against iron wire, proceed as follows: Clean the wire by rubbing it with emery cloth and then with filter paper. Form it into a spiral by wrapping it around a clean glass rod and cut the spiral into lengths weighing about 0.4 gram. Throw away the part of the wire which was held by the fingers. Accurately weigh the pieces and put them into small Erlenmeyer flasks of about 75-c.c. capacity. Close each flask by a small glass bulb with the stem reaching down into each neck. The glass bulb prevents air entering the flask and oxidizing the iron. Add 30 c.c. of H_2SO_4 (1:4) and set the flask on a hot plate until the iron dissolves, avoiding violent boiling. When the iron is completely dissolved, pour cold water over the bulb into the flask, thus washing both the bulb and the neck of the flask. Transfer the solution to a beaker, dilute to 200 c.c. and titrate without delay. The weight of the wire taken multiplied by the iron factor of the wire and divided by the number of cubic centimeters of the permanganate used will be the amount of iron equivalent to 1 c.c. of the permanganate. The result may be checked by running the titrated solution through the reductor and again titrating. With the "blank" deducted, the results ought to check. The wire is usually about 99.8 per cent iron.

Now, knowing the strength of the solution, it may be diluted so that 1 c.c. will just equal 0.0100 gram of iron. The water used for diluting should have been boiled and, while boiling, treated with permanganate until it retained a very faint pink color.

In all work involving the use of permanganate, glass stopcocked burettes should be used, as permanganate is reduced by rubber.

To standardize with ferrous ammonium sulfate or sodium oxalate, weigh 0.4799 gram of the oxalate previously dried at 130°C. cr 2.81 grams of the sulfate unheated, transfer to a 300-c.c. flask, add 250 c.c. of hot water containing 8 c.c. of strong H_2SO_4 and titrate not too rapidly, approaching the end point slowly. In the case of the oxalate the titration should be carried on at 70°C.

Standard sodium oxalate and standard iron ore may be obtained from the U. S. Bureau of Standards. The amounts of sulfate and oxalate given above are each equal to 0.400 gram of iron. The reason this amount is chosen is that it is about the amount of iron that will ordinarily be titrated in a sample of ore and, consequently, no end point correction will have to be made. The end color obtained in standardization should be of the same depth as when a sample of ore is titrated.

Titrating Solution.—This is made by dissolving 160 grams of manganous sulfate in water, diluting to 1,750 c.c., adding 330 c.c. of phosphoric acid and 320 c.c. of sulfuric acid. Use the concentrated "syrupy phosphoric acid" of 1.725 sp. gr.

Preparation of the Reductor.—A simple form of the reductor is shown in Fig. 5. The large tube is about ⅝ in. inside diameter and is contracted at the bottom and expanded into a funnel at the top. The stem enters the rubber stopper of the flask, which is connected to a suction pump. The tube is filled as follows: A plug of glass wool is placed in the bottom. Above this is ¾ in. of clean white sand *B*, which has been boiled with HCl and then washed to remove the iron. Above the sand is a disc of perforated platinum *C*. Above this the tube is filled for 10 in. with granulated zinc of such size that it will pass through a 20-mesh sieve but not through a 30-mesh. It should be amalgamated as follows: Moisten a quantity of it with very dilute H_2SO_4 (about 3 c.c. to 100 c.c. of water), add a small drop of mercury and stir it in until the zinc shows uniformly the white mercury color. Wash the zinc free from acid and put it in the tube. Avoid more than just enough mercury; ½ gram is sufficient for 150 grams of zinc.

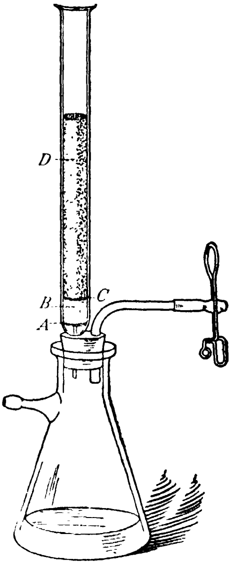

Fig. 5.

The solution to be reduced is poured into the funnel-shaped top of the reductor. The rate at which it is drawn through must not be too rapid. Test this point by drawing an iron solution through and then adding some ammonium sulfocyanate to the reduced solution. If this gives a pink color the speed was too great and must be reduced by diminishing the suction. If the rate is too fast it can be reduced by opening the pinch-cock. If air is drawn through the zinc in the reductor and immediately followed by dilute acid, the liquid running through is sometimes found to be oxidizing, possibly from the formation of H_2O_2; hence, while running through the solution and wash water, the surface of the zinc must be kept continually covered with liquid.

If the reductor has stood unused for some time it should be washed out with dilute sulfuric acid and water before putting the solution through it.

Process of Analysis.—Weigh out 1 gram of the finely ground sample and ignite it in a porcelain crucible to destroy organic matter. Transfer it to a small beaker, add 10 c.c. of concentrated HCl, cover and digest till all the iron is in solution. Add 20 c.c. of dilute H_2SO_4 (1:1) and boil gently to expel some of the excess of HCl, then dilute to about 100 c.c. and filter, washing the residue thoroughly. Dilute the filtrate to 250 c.c., using cold water, as the solution should be cool.

Now pour the solution into the zinc reductor and apply such suction that the liquid will flow through in a moderate stream. Follow the solution with 100 c.c. of 5 per cent H_2SO_4, then with 150 c.c. of water, keeping the zinc covered with liquid during the entire process so that air will not be drawn through the zinc. As soon as the last wash water has passed through, disconnect the suction tube, pour the solution into a large beaker and rinse the flask out with a little water. Add 10 c.c. of the titrating solution and titrate with $KMnO_4$. The number of cubic centimeters of the $KMnO_4$, times the iron factor, times 100 equals the percentage of iron.

Notes on the Process.—Ignition of the sample is necessary unless organic matter is known to be absent.

The gentle boiling, after adding the dilute H_2SO_4, gets rid of most of the HCl. It is not necessary to expel all of it.

Determine the correction of the impurity in the zinc by running a blank with the same amount of water and acids used in the analysis, and deduct the volume of permanganate required in this from that used in the analysis.

The process should be checked on ores of known composition.

THE PERMANGANATE METHOD WITH REDUCTION BY STANNOUS CHLORIDE

This method is reliable, provided the conditions of titration are strictly controlled. A very slight excess of $SnCl_2$ must be used; the amount of HCl present must not be more than is directed; the solution to be titrated must be cold and dilute. In strongly acid solutions $HgCl$ and HCl are acted upon by permanganate. The permanganate should not be added too rapidly, especially toward the end. Organic matter and sulfides must be destroyed by ignition of the ore.

Process of Analysis.—Weigh 1 gram of the finely ground ore, transfer it to a crucible and ignite to redness. Transfer to a beaker, add 20 c.c. of HCl (1:1). Heat until the iron is all dissolved. To hasten the solution, $SnCl_2$ may be added at this point until the solution becomes colorless. Now if an excess of $SnCl_2$ has been added, add permanganate until the yellow color of ferric iron appears, then to the hot solution very carefully add $SnCl_2$ solution until the yellow just disappears. *Cool thoroughly,* add 10 c.c. of saturated $HgCl_2$ solution, stir well and allow to stand for several minutes. Dilute to 250 c.c. with water free from reducing matter, add 10 c.c. of the "titrating solution" and titrate not too rapidly with permanganate. Approach the end point rather slowly. The last drop should give a persistent pink color.

Note.—Instead of using $SnCl_2$, zinc, aluminium or SO_2 can be used to reduce the iron, and then, according to Hough, the only reagent necessary to add to make the titration accurate is phosphoric acid.

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DETERMINATION OF FERROUS OXIDE IN IRON ORE

This determination is not frequently called for, but in the case of carbonate ore, $FeCO_3$, or magnetite ore, Fe_3O_4, it is sometimes necessary in order to calculate the heat balance of a blast furnace. The ferrous oxide is also determined to test the completeness of calcination of carbonate ore.

When ores of iron are dissolved in HCl, ferric oxide goes in solution as $FeCl_3$ while ferrous oxide or ferrous carbonate goes in solution as ferrous chloride. Thus:

$$FeCO_3 + 2HCl = FeCl_2 + H_2O + CO_2.$$

The $FeCl_2$ can then be titrated by any of the ordinary methods.

An accurate determination of ferrous oxide can be made only when certain possible constituents of ores are absent. Some organic material, and all decomposable sulfides, will reduce ferric to ferrous iron and cause the results to run high. On the other hand, any MnO_2 such as pyrolusite, will liberate chlorine when the ore is dissolved in HCl and this will oxidize the ferrous iron to ferric, making the results for FeO low.

Process of Analysis.—Fit a 150-c.c. flask with a clean rubber stopper perforated with one hole, in which is inserted a piece of glass tubing 2 in. long. Upon this slip a piece of pure gum tubing 3 in. long closed at one end with a glass rod. In the space between the tube and rod make a vertical slit ½ in. long with a sharp knife. This acts as a valve which keeps out the air and yet lets out the evolved gases. It is necessary to keep out the air to prevent it from oxidizing any ferrous iron.

Put in the flask 1 gram of Na_2Co_3 and add HCl at such a rate that the liquid will not froth out of the flask. When the carbonate is all dissolved, place the stopper in the flask. Weigh out 1 gram of finely ground ore, transfer to the flask, add a small pinch of carbonate, and then 25 c.c. of strong HCl. Quickly insert the stopper and heat to boiling, and keep at a boiling temperature until the ore is dissolved. Add 200 c.c. of oxygen-free water and titrate with standard dichromate solution. The iron value of the dichromate multiplied by 1.2866 gives the amount of FeO in the ore.

The Electrometric Titration of Iron.—Instead of using chemical indicators, the end point in the determination of iron may be very accurately obtained by electrometric means. See page 252.

CHAPTER IV

THE DETERMINATION OF PHOSPHORUS IN IRON ORES, IRON AND STEEL

The methods in general use all depend upon first getting the phosphorus into solution, as orthophosphoric acid, and then separating it from the iron and other bases in the form of ammonium phosphododecamolybdate, the so-called "yellow precipitate."

The phosphorus in this is then determined directly or indirectly, and either gravimetrically or volumetrically.

To determine the phosphorus, the yellow precipitate may be dried and weighed as such, or it may be ignited to $P_2O_524MoO_3$ at a temperature of 450°C. for ten minutes, or the phosphorus may be determined in the yellow precipitate by volumetric methods; thus it may be reduced by nascent hydrogen to $Mo_{12}O_{19}$, which is then oxidized by standard permanganate back to its original condition. Or the yellow precipitate, which is an acid anhydride, may be titrated by standard alkali. Lastly, the yellow precipitate may be dissolved in ammonia, and the phosphorus precipitated with magnesia mixture and weighed as magnesium pyrophosphate.

The complete deposition of phosphorus as ammonium phosphomolybdate is often delayed, and under some conditions prevented, by such elements as vanadium in the quinquivalent condition, titanium, zirconium and fluorine. The purity of the phosphomolybdate precipitate is often a matter of doubt. It is well known that the first three elements named, as well as silicon and arsenic, are carried down completely, or in part, by the precipitate. The researches of Hundeshagen and others have demonstrated that the composition of ammonium phosphomolybdate varies with such factors as temperature, concentration of the molybdate reagent and the acidity of the solution.

Losses are chiefly occasioned by the neglect or improper treatment of insoluble compounds obtained during the course of the analysis. These frequently contain phosphorus, and they are often caused by titanium; they will be encountered when such elements as zirconium, tin, titanium or tungsten are present, when the phosphomolybdate is dissolved on a filter paper with NH_4OH, as their phosphates are white, and not easily seen on the paper.

It is difficult to extract all the phosphorus from insoluble phosphates by means of alkali carbonate fusions followed by water extractions. It is not possible, for example, to recover all of the phosphorus from 0.1 gram of zirconium or titanium phosphates by two careful carbonate fusions followed by water extractions.

Compounds containing phosphorus must not be subjected to protracted fusions with alkali pyrosulfate in open crucibles and at unnecessarily high temperatures. Negligible losses occur in short fusions when crucibles are tightly covered and only sufficient heat for proper fusion is used. Such fusions may, however, give rise to meta- or pyrophosphates, which must be converted to orthophosphate before further treatment.

Phosphorus is precipitated with tungstic acid, and the recovery of it from small amounts of tungstic acid is carried out as with the non-volatile residue after the purification of silica. With larger amounts of tungsten the phosphorus is more conveniently recovered and the tungsten at the same time eliminated by dissolving the tungstic acid in ammonium hydroxide, slightly acidifying with hydrochloric acid, adding 1 gram of alum, and then precipitating the phosphorus together with aluminium by the addition of ammonium hydroxide in the *slight* excess prescribed by Blum, boiling and filtering.

The complete precipitation of phosphorus as aluminium or iron phosphate requires at least a fivefold excess of aluminium and a tenfold excess of iron and the use of only a *very slight* excess of ammonia. A large excess of ammonia is to be avoided even when iron and aluminium are greatly preponderant.

As mixtures of sulfuric and phosphoric acids lose phosphorus when heated at high temperatures to complete expulsion of sulfuric acid, any hydrofluoric acid treatment of silica containing phosphorus should be done with nitric instead of sulfuric acid and the hydrofluoric acid expelled by repeated treatment with it. In this connection it is imperative that any final evaporation of phosphoric-sulfuric acid solutions be carried on at as low a temperature as possible and be stopped as soon as fumes of sulfuric acid appear.

The yellow precipitate, when dried at 130°C., has the composition $(NH_4)_3PO_4 12MoO_3$. This formula requires 1.65 per cent of phosphorus. The average of many most carefully conducted experiments has shown that the precipitate, if free from admixed molybdic acid or other impurities, contains 1.63 per cent phosphorus within very narrow limits.

The precipitate is only obtained pure when formed under very exact conditions, and is easily affected by subsequent treatment, so that all methods depending upon the weighing of the yellow precipitate or its volumetric determination must be carried out rigorously according to the prescribed directions in every detail.

When a solution of ammonium molybdate in nitric acid is added to an acid solution containing phosphoric acid, the whole of the phosphoric acid is precipitated as the yellow ammonium phosphomolybdate, under the following conditions:

All the phosphorus must be present as tribasic (ortho) phosphoric acid.

The precipitation should always be performed in a solution containing nitric acid, as the precipitate is less soluble in nitric than hydrochloric or sulfuric acids. A wide range in the concentration of nitric acid is permissible. Satisfactory technical analyses can be had in the presence of as much as 10 per cent by volume of hydrochloric acid or 5 per cent by volume of sulfuric acid, through the use of double the amount of molybdate reagent ordinarily employed (100 as against 50 c.c.) and a longer precipitation period (30 as against 15 to 20 minutes). In the case of hydrochloric acid, complete precipitation is obtained when the solution is allowed to stand overnight; complete precipitation is not possible with sulfuric acid, which must be avoided or used sparingly and then converted into ammonium sulfate in accurate analyses. Hydrofluoric acid retards the precipitation of phosphomolybdate and causes the formation of a more soluble precipitate; both difficulties can be entirely prevented by converting the acid to fluoboric acid by the addition of borax or boric acid.

The temperature of the solution has a decided bearing on the precipitation. Precipitation at low temperatures (10 to 20°C.) is slow and the precipitates are difficult to filter and wash. Precipitations at 40 to 50°C. are more rapid and the precipitates are in better condition. Higher temperatures, such as 80 to 90°C., give rapid precipitation, but the precipitates are richer in MoO_3 and more contaminated by elements such as arsenic.

Ammonium nitrate has a beneficial effect, as it causes more rapid precipitation and a coarser grained precipitate. The precipitate is slightly soluble, however, in a large excess of ammonium nitrate and it should preferably be present in amounts not over 15 per cent. Ammonium chloride and sulfate are not as desirable, as they tend to delay precipitation and have slightly greater solvent action on the precipitate. Their presence in reasonable amount is not harmful if a greater excess of the molybdate precipitant is used.

A large excess of the molybdate precipitant is required. This excess varies from ten times the theoretical amount in a nitric acid-ammonium nitrate solution of pure orthophosphoric acid to a fifteen to twenty-five-fold excess in ordinary solutions, and a forty to sixty-fold excess in solutions containing substances which retard the precipitation.

The yellow precipitate is insoluble in the solution of ammonium molybdate in nitric acid; also in solutions of ammonium salts, if neutral or only very slightly acid, but if strongly acid they attack the precipitate, which is, however, reprecipitated by the addition of molybdic acid solution to the liquid. It is also practically insoluble in a solution of potassium nitrate when neutral and not too dilute. Solutions of salts of organic acids usually dissolve the precipitate to some extent. From these solutions nitric acid and ammonium nitrate, in some cases, reprecipitate the compound, in others, *e.g.*, with tartaric acid or oxalic acid, probably not completely.

The mineral acids, HCl, HNO_3, H_2SO_4, all have a solvent action on the precipitate even in the presence of ammonium nitrate. HNO_3 has the least, HCl probably the most.

Pure water is said to decompose the precipitate to a slight extent and make it run through the filter.

Precipitation is much more rapid from hot than from cold solutions, but in time it is probably complete at any temperature. The precipitate from hot solutions is denser and more crystalline; from cold, finer and more granular, and harder to filter and wash.

Agitation greatly accelerates precipitation in this as well as in other chemical reactions.

The precipitate dried to constant weight at ordinary temperatures retains a little acid and water, which it loses when dried at 130°C. By washing the precipitate with a neutral solution of ammonium or potassium nitrate or by prolonged washing with water, it can be freed from acid without drying.

Silicic acid in the solution does not seem to interfere with the complete precipitation of phosphorus as yellow precipitate, but a trace of the SiO_2 usually comes down with the precipitate, especially if the solution is too concentrated or too warm, or stands too long. If the solution is rather dilute, not too hot and is filtered promptly, the yellow precipitate can be obtained in the presence of considerable SiO_2 and practically free from it. Titanic acid does not prevent, though it greatly delays, the precipitation of phosphorus by molybdic acid solution.

Organic matter has usually been supposed to interfere with the precipitation of phosphorus, but it is probable that in many cases, noticeably in steel analysis, the bad results attributed to this cause were due to the fact that the phosphorus had not all been converted into the tribasic acid. The pyro- and metaphosphoric acids are not completely precipitated by molybdic acid solution.

When arsenic acid is present in the solution with the phosphorus, some of it will be precipitated at the same time, the amount increasing with the temperature. Only very small amounts come down at temperatures not exceeding 25°C.

MoO_3 may separate with the yellow precipitate as a light crystalline deposit. This free MoO_3 is soluble in acids with difficulty and cannot be washed out of the yellow precipitate. Its separation must always be guarded against when the yellow precipitate is to be weighed or titrated. It forms when the solution contains too much MoO_3, is too concentrated or too dilute, too strongly acid or too nearly neutral. Too high a temperature precipitates it. The addition of strong nitric acid to a solution of molybdic acid will sometimes precipitate it, as will the adding of molybdic acid solution to solutions of iron in concentrated nitric acid. Long standing favors the separation of excess MoO_3 with the yellow precipitate. A finely divided form of the MoO_3 sometimes separates, easily mistaken for the yellow precipitate and liable to escape notice.

Besides the MoO_3, the yellow precipitate may be contaminated by ferric molybdate or ammonium metamolybdate, which are precipitated by too long digestion or too high temperature. If the precipitate stands at a temperature not exceeding 40°C., contamination in this way is not apt to occur.

When the yellow precipitate is thrown down in a solution containing much iron and not sufficient acid, basic iron salts are likely to accompany it, making it reddish in color. This is especially the case when the solutions are hot.

The yellow precipitate, if pure, is easily and completely soluble in ammonia (if it contains iron, the solution will be turbid from the formation of ferric phosphate). From this solution the phosphoric acid is completely precipitated by magnesia mixture as $MgNH_4PO_4$. If the yellow precipitate contains any SiO_2, this will also, in part at least, dissolve in the ammonia and separate with the magnesia precipitate, making it a little flocculent. By cautiously adding HCl to the ammonia solution of the yellow precipitate until nearly neutral and letting it stand for some time in a warm place, the silica separates and may be filtered off. The phosphorus may then be precipitated in the filtrate. In precipitating phosphoric acid with magnesia mixture, add the reagent drop by drop and stir the liquid constantly, so that the precipitate separates slowly and in a crystalline form. Otherwise it will be impure, containing magnesia in excess and molybdic anhydride. The magnesium pyrophosphate must be ignited thoroughly and with access of air to drive off any trace of MoO_3 it may contain.

If the sample to be analyzed contains vanadium, the yellow precipitate will be contaminated with it, making the precipitate more soluble. When vanadium is present, the precipitate will have an orange color instead of being yellow.

Since *complete* precipitation of the phosphorus as *pure* ammonium phosphomolybdate with constant composition is only possible under certain closely controlled conditions, it is necessary for the chemist to find out for himself by repeated experiment exactly what these conditions are, and to standardize his solutions and make his determinations under exactly the same conditions, keeping in mind the many things which may cause error.

It is evident that correct determinations of phosphorus can be obtained only by methods which call for solution of the phosphomolybdate and reprecipitation of the phosphorus as a pure compound of definite composition. By far the most satisfactory of such methods calls for solution of the washed phosphomolybdate in dilute ammonium hydroxide, reprecipitation of the phosphorus as magnesium ammonium phosphate, and ignition of this to the pyrophosphate. In this method the composition of the phosphomolybdate is immaterial; it is only necessary that all the original phosphorus be present as orthophosphate in the solution which is treated with magnesia mixture, and that the resulting magnesium ammonium phosphate be pure and of definite composition.

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DETERMINATION OF PHOSPHORUS WITH FINAL WEIGHING AS MAGNESIUM PYROPHOSPHATE

This method is free from the chances of error due to the presence of impurities in the yellow precipitate. It is gravimetric and the phosphoric acid is finally weighed in a form not subject to variation in composition if care is taken in the precipitation. It is applicable to all kinds of material, and to any percentage of phosphoric acid; hence, it is a standard method to which final reference must be made in all important determinations.

A pure magnesium-ammonium phosphate of definite composition can be easily obtained from ammoniacal solutions of small amounts of pure ammonium phosphomolybdates, provided the solutions—preferably of a volume not to exceed 50 to 75 c.c.—are slightly acidified with hydrochloric acid, treated with 0.2 to 0.5 gram of citric acid, a five- to ten-fold excess of magnesia mixture, and then carefully neutralized with ammonium hydroxide (sp. gr. 0.90), slowly added dropwise and with constant stirring until the precipitate begins to form and then in an excess of 3 to 5 per cent by volume. A three- to four-hour digestion period is ordinarily sufficient but a 24-hour period does no harm and is desirable when small precipitates are involved. The most desirable washing solution is one containing 3 to 5 per cent by volume of ammonium hydroxide (sp. gr. 0.90). No advantage is gained by using stronger washes or ones containing ammonium nitrate. The precipitate may be ignited either wet or dry, and in either platinum or porcelain. The chief precaution in igniting the precipitate lies in first *warming* until any water in the paper or precipitate is given off, then *slowly charring* the paper without actual flaming in an oxidizing atmosphere, then igniting at as low a temperature as possible, and with the lid placed to allow circulation of air, until the carbon has been destroyed and the residue is white, and finally at approximately 1,000°C. with the crucible covered to constant weight.

Process for Iron Ores.—(In the absence of more than traces of titanium or arsenic.) Weigh 1 to 5 grams, depending upon the percentage of phosphorus, of the very finely pulverized ore. Put it into a 4-in. porcelain dish or casserole, add 1 c.c. nitric acid, then concentrated HCl, using 10 c.c. for each gram of ore taken, and then add 15 c.c. more, cover with a watch-glass, warm until all the iron appears to be in solution, then boil down to dryness, keeping covered to avoid spattering. Dry on a hot plate until the acid is expelled, then add from 30 to 50 c.c. of concentrated

HCl, cover and digest until all the iron is dissolved. Now boil down until the liquid is syrupy. If the dish is kept covered, there need be no formation of dry salt on the sides. Add 50 c.c. of 1:2 HNO_3, washing off the cover and sides of the dish. Filter into a 250-c.c. beaker, using a small filter; transfer the residue to the filter and wash until there is no acid taste to the washings.

Dry and ignite the residue. With ordinary ores, if light colored and not too large in amount, it is generally practically free from phosphorus, and may be thrown away. In case the ore is an unknown one, and occasionally even on known ones, the insoluble residue should be fused with sodium carbonate, the fusion dissolved in HCl, evaporated to dryness and heated to dehydrate the silica. Dissolve the residue in 2 or 3 c.c. of HCl and 10 c.c. of water and filter into the beaker containing the main filtrate.

Instead of proceeding as above, the filtrate from a silica determination may be used for the determination of phosphorus. The filtrate should not much exceed 100 c.c.

Heat if necessary to 80°C. and add from a pipette, and with vigorous stirring, 100 c.c. of molybdate solution. Stir the solution vigorously for several minutes more. Vigorous stirring greatly lessens the time required for precipitation. Allow to stand until the liquid is clear and the precipitate has all settled (this should not require more than one hour); remove a portion of the clear liquid with a pipette and test it by adding a little more molybdic acid solution and warming, to make sure that all the phosphoric acid is precipitated.

Filter the liquid through a 7-cm. filter. Transfer the precipitate to the filter and wash free from iron, with a cold 1 per cent solution of HNO_3. The washing must be thorough or difficulty will be experienced when dissolving the precipitate, as phosphates of iron and aluminium may form and clog up the filter. When the precipitate is washed, put the beaker in which the precipitation was made under the funnel and redissolve the precipitate on the filter with 20 to 30 c.c. of a solution made by dissolving 20 grams of citric acid in 100 c.c. of water and adding NH_4OH until the solution is strongly alkaline. When it is dissolved and the liquid has all run through, wash the filter three or four times with water, then with a little dilute HCl, to dissolve any ferric or other insoluble phosphate present, and finally with water. Use care in washing, letting each portion of water run through before adding another, so as to keep the volume of the filtrate small. This should not exceed 100 c.c. and is usually less. The filtrate should now be clear and colorless. If the alkaline solution of the phosphomolybdate should be cloudy, heat to boiling and filter through the same paper as before, wash and save the paper.

Make the filtrate acid with HCl, add a considerable excess of the magnesia mixture, judging the amount from the size of the "Y.P.," usually 10 c.c. Add NH_4OH with vigorous stirring until the solution is alkaline, then add 5 c.c. more. Continue to stir the solution vigorously for four or five minutes. Let it stand until the precipitate of $MgNH_4PO_4$ has settled completely (three or more hours). The precipitate should be white and crystalline; if red or flaky, the results will be inaccurate. Filter on a small filter or, better, on a Gooch perforated crucible. Wash with water containing one-tenth its volume of concentrated NH_4OH and a little NH_4NO_3, dry, ignite very slowly and carefully and weigh as $Mg_2P_2O_7$. This contains 0.2787 of phosphorus.

It is essential that the filtrate from the phosphorus precipitate should give at once a strong reaction for magnesium when tested with a drop of a solution of sodium phosphate, as a considerable excess of reagent is necessary to precipitate the phosphorus completely.

Instead of weighing the phosphorus as $Mg_2P_2O_7$, the phosphorus molybdate may be titrated by the alkali or permanganate methods, as on pages 58 and 60.

When the ore contains appreciable amounts of titanium, zirconium or tin and, in general, when the most accurate results are necessary, the procedure must be modified as follows:

Weigh out the ore and dissolve it in HCl as in the regular process. If the filtrate from the insoluble residue is not clear, add a little HNO_3 and warm, which will probably clear it. If a slight turbidity remains, it is of no importance and may be neglected. Now proceed with the filtrate as in the regular process. After the yellow precipitate has been dissolved in ammonia and the filter washed as directed, dry and burn the filter and add the ash to the insoluble residue. This is necessary, as insoluble compounds of phosphorus and titanium may be retained in the filter. The filtrate is combined with the similar one obtained from the "Y.P." from the fusion. This residue is now mixed with eight times its weight of dry Na_2CO_3 and fused as for silica. Boil the fusion with water until thoroughly disintegrated. The phosphorus passes into solution as phosphate; while the TiO_2 remains insoluble as titanate. Filter the liquid from the insoluble matter, acidulate the filtrate with HNO_3 and evaporate to dryness. Add a little HNO_3, then water and filter from the separated SiO_2.

Proceed as usual until the $MgNH_4PO_4$ precipitate is obtained from the combined solutions of the two phosphomolybdate precipitates. Filter, keeping most of the precipitate in the flask and wash with dilute NH_4OH.

Dissolve the $MgNH_4PO_4$ on the filter in 25 c.c. of dilute hydrochloric acid (1:1), catching the solution in the original flask containing the bulk of the precipitate. Wash the filter thoroughly with dilute hydrochloric acid (5:95). Transfer the solution to a 200-c.c. beaker. In case the amount of arsenic is known to be very small, add 0.5 to 1 gram of ammonium bromide and boil the hydrochloric acid solution to a volume of 5 to 10 c.c. Where large amounts of arsenic were originally present, treat with hydrogen sulfide, digest, filter and wash with acidulated hydrogen sulfide water. Boil to expel hydrogen sulfide and to reduce the volume to 50 to 75 c.c. Add 0.1 to 0.2 gram of citric acid, 2 to 3 c.c. of magnesia mixture, make ammoniacal as above and allow to stand in a cool place for four to twenty-four hours.

Filter, wash with dilute ammonium hydroxide (1:20) and ignite the precipitate carefully and at as low a temperature as possible until the carbon has been destroyed and the residue is white. Finally, ignite at approximately 1,000°C. to constant weight. Dissolve the ignited residue in 5 c.c. of dilute nitric acid (1:1) and 20 c.c. of water. Filter, wash the residue with hot water, ignite and weigh. Treat with a few drops of hydrofluoric acid, evaporate to dryness, ignite and reweigh. Subtract any loss of weight from the original weight of the pyrophosphate and calculate on the basis of this purified magnesium pyrophosphate.

Solutions Required. Molybdate Solution.—Johnson's directions for preparing the solution are as follows:

Into a large evaporating dish weigh 110 grams of ammonium molybdate and 100 grams of ammonium nitrate, and add 80 c.c. of ammonium hydroxide (0.95 sp. gr.). Dilute to 1,400 c.c. with water. Heat for about 30 minutes, stirring once in a while until all salts are in solution. Dilute to 4,000 c.c. with water. Let stand overnight. Filter the insoluble material through double 15-cm. papers. *Do not wash.* The clear solution thus obtained should remain clear indefinitely.

Magnesia Solution.—Dissolve 50 grams of $MgCl_2.6H_2O$ and 100 grams of NH_4Cl in 1 liter of distilled water, or 65 grams of $MgSO_4.7H_2O$ and 100 grams of ammonium chloride in 1 liter of water. Of this solution 10 c.c. will precipitate about 0.07 gram of phosphorus.

DETERMINATION OF PHOSPHORUS IN BLACK BAND AND OTHER ORES WHICH CONTAIN MUCH CARBONACEOUS MATTER

These should be weighed out in a porcelain crucible and ignited, taking care not to heat so rapidly as to cause loss by blowing out of fine particles. Set the crucible on its side over a small flame and let the material gradually burn away until all carbon is gone, and an "ash" is left. Treat this by the regular process. Avoid a high temperature in burning or the material will *cake,* thus delaying the combustion and leading to imperfect solution. A dull red-heat is sufficient.

DETERMINATION OF PHOSPHORUS IN MILL CINDER

Two points here need attention. First, since the material is a soluble silicate, it should be decomposed by weak acid and evaporated to dryness as in the determination of silica after fusion. Second, all mill cinder contains particles of metallic iron, in which phosphorus is present as phosphide. These would evolve PH_3 gas when dissolved in HCl, so HNO_3 must be used to oxidize this phosphorus.

Proceed as follows: Weigh 1 gram into a porcelain dish, add 20 c.c. HNO_3 (1.2 sp. gr.), stir well to prevent caking and warm till action ceases, then add 10 c.c. H_2O and 10 c.c. concentrated HCl. Evaporate to dryness and heat on an iron plate to 200°C. for half an hour. Add 10 c.c. HCl, and digest until all the iron is dissolved. Dilute, filter and proceed as with an ore.

DETERMINATION OF PHOSPHORUS IN IRON AND STEEL

The phosphorus in iron and steel exists principally as *phosphide.* When these metals are treated with ordinary oxidizing solvents, such as dilute HNO_3, or $KClO_3+HCl$, the oxidation of the phosphorus is incomplete. Even concentrated HNO_3 fails to convert all the phosphorus into tribasic phosphoric acid. The metal must not be dissolved in HCl or H_2SO_4, as they would cause phosphorus to pass off as phosphine gas (PH_3).

These metals also contain carbon compounds which pass into solution in HNO_3, forming a dark-colored substance, and the presence of this dissolved carbonaceous matter is generally supposed to interfere with the precipitation of the yellow precipitate. It seems probable, however, from certain experiments that, if the phosphoric acid is in the tribasic state, this organic matter is without influence. It is certain, however, that, unless the oxidizing action is strong enough to destroy this carbonaceous matter completely, the phosphorus is not all oxidized and hence not precipitated completely.

The oldest and most certain method of oxidation is the "dry oxidation method." It consists in dissolving the metal in HNO_3 either concentrated or dilute (sp. gr. 1.2), and then evaporating the solution to dryness. The dry mass of basic ferric nitrate is then heated to about 200°C. for some time. At this temperature the salts are decomposed, the iron largely converted to ferric oxide, and the dissolved carbon and the phosphorus completely oxidized. This residue can then be dissolved in HCl and treated like an ore. The method is always reliable and involves no delicate adjustments.

To save the time required for evaporating the solution and baking the residue, several methods have been devised for oxidizing the material in the nitric acid solution. The reagents most successfully used are potassium permanganate, chromic acid and ammonium persulfate. Aqua regia, potassium chlorate or chlorine fail to oxidize the material completely.

When permanganate is used there is a separation of MnO_2 as a brown precipitate which holds phosphorus and must be entirely redissolved before filtering from the residue or precipitating the phosphorus. This is accomplished by adding a reducing agent, such as oxalic acid, ferrous sulfate, sugar or potassium nitrite, to the acid liquid. Any considerable excess should be avoided. The MnO_2 is reduced to MnO and dissolved in the acid.

Wet methods are more rapid but are not adapted to all kinds of material and must only be used where they have been shown to apply by repeated checking of the results with the standard methods.

When pig iron or steel, containing silicon, is dissolved in HNO_3, evaporated and "baked," the HCl solution of the residue will be found to filter very slowly because silicic acid in HNO_3 solution is not fully dehydrated on evaporation, even if the residue is heated to 200°C. Hence, when the residue is treated with HCl, some of the SiO_2 goes into the solution and leaves the rest in a highly gelatinous form.

The SiO_2 left after the evaporation of an HCl solution is much more granular and easily filtered off. Therefore, in all cases where silicon is present to any extent the HCl solution of the "baked" residue should be evaporated to hard dryness and again taken up in HCl. This second evaporation takes but little time and is essential, especially with cast iron, if a long and tedious filtration is to be avoided.

After the phosphomolybdate precipitate is obtained, the final process may be any one of the following: the precipitate is dried and weighed, or titrated with a standard alkali solution, or it may be reduced by nascent hydrogen and then titrated by a standard permanganate solution or, finally, the phosphorus may be precipitated as $MgNH_4PO_4$ and weighed.

Process of Analysis.—Weigh 1 or 2 grams, depending upon whether the phosphorus content is above or below 0.15 per cent, transfer the sample to a 250-c.c. Erlenmeyer flask, add 50 c.c. of HNO_3 (sp. gr. 1.13) and heat until the sample is all decomposed. (If the sample is pig iron, a large residue of graphite will be left.) Add 1 gram of ammonium persulfate and boil until combined carbon is completely oxidized. Filter and wash the residue with a 2 per cent nitric acid solution until no iron stain is left on the filter paper. Heat the filtrate to boiling and add a 2 per cent $KMnO_4$ solution until there is a slight excess of the permanganate and continue boiling until the excess is decomposed and precipitated as MnO_2, cool somewhat and add potassium nitrite (KNO_2) until the MnO_2 just dissolves, and continue boiling for a minute to remove the brown nitrous oxides. Cool the solution to 70°C., add 50 to 100 c.c. of ammonium molybdate solution and shake the flask for five minutes. Allow the precipitate to settle for a half hour or until the supernatant solution is clear. Filter through a 9-cm. filter paper, transfer the precipitate to the filter paper and wash with the appropriate wash solution as given below.

Gravimetric Method.—This method is generally used as a "rapid method." It is not, however, as rapid as the volumetric method for phosphorus, but it is the most rapid of the gravimetric methods.

Since accurate results by this method depend upon purity of the yellow precipitate, and uniform composition of the same, it is necessary that the conditions of precipitation be strictly controlled and that the process be checked by running the phosphorus in a standard sample under exactly the same conditions as obtain in the routine work of the laboratory.

The yellow precipitate is quite hygroscopic, hence it must be weighed promptly and with the least possible exposure to the air.

As the yellow precipitate has 1.63 per cent of phosphorus, it is convenient to take that amount in grams for analysis. The drying and weighing of more than 0.4 gram of yellow precipitate is difficult, hence for ores having over 0.4 per cent of phosphorus, take one-half of the above amount (0.815).

Prepare a Gooch filter as follows: Pour into a Gooch crucible an amount of properly prepared asbestos fiber so that when the asbestos is sucked tightly on the bottom of the crucible by means of a suction flask a mat about one-thirty-second of an inch thick is formed. Wash the mat with a 1 per cent nitric acid solution, place the crucible in an oven and dry at 110°C. Fifteen minutes is usually enough. Cool in a desiccator and weigh. Filter the phosphomolybdate precipitate on the mat in the crucible, using the suction flask, transfer all the precipitate to the crucible, wash 15 times with 1 per cent nitric acid solution and again dry the crucible and contents in the oven at 110°C. Cool in a desiccator and weigh. The increase in weight multiplied by 0.0163 gives the amount of phosphorus in the sample.

Emmerton's Method. Titration by Permanganate.—When the yellow precipitate is dissolved in NH_4OH and mixed with a very considerable excess of H_2SO_4, it all remains in solution. If this solution is warmed with metallic zinc, zinc dissolves, and the molybdic acid is rapidly reduced, giving first a dark red and finally a green solution containing, if the reduction is complete, Mo_2O_3. If this solution is rapidly filtered from any undissolved zinc, it can be titrated with a solution of potassium permanganate, which promptly oxidizes the Mo_2O_3 back to MoO_3. The solution becomes colorless and, finally, when oxidation is complete, is colored pink by the least excess of permanganate.

The color of the reduced solution depends somewhat upon the excess of sulfuric acid present. If this is too large, the green color will not be reached and the end of the reduction cannot be determined. The smaller the excess of H_2SO_4 the sharper is the change from red to green at the end.

Complete reduction is a matter of considerable difficulty and the methods in use do not always attain it. This has given rise to the assigning of various formulas to the reduced product. Emmerton gives $Mo_{12}O_{19}$, which probably most nearly represents the usual product of the reduction method he describes. The reductor gives ratios between the molybdenum and the oxygen which vary with the methods of using it. Blair and Whitfield give for the reductor product $Mo_{24}O_{37}$.

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This uncertainty as to the reduction product makes the standard permanganate solution of uncertain value in phosphorus if standardized against metallic iron only; hence, it is better to check it against a standard steel, ore or pig iron, of known phosphorus content which should be treated exactly by the method used in the regular analysis.

The widely extended use of this method shows, however, that, although there is some uncertainty as to the nature of the oxide produced by reduction, this possibly being different for different workers, by working always in exactly the same way, the reduction is uniform, and hence the titration is a reliable method for estimating the yellow precipitate, and indirectly the amount of phosphorus.

Process of Analysis.—Wash the flask and phosphomolybdate a half-dozen times with a 1 per cent nitric acid solution, then ten times more with 1 per cent sulfuric acid solution, or until every trace of HNO_3 and iron is gone. Now set the funnel in the flask and dissolve the precipitate back into it with dilute NH_4OH (1:4), using altogether 30 c.c. To save time, some chemists puncture the filter and wash the precipitate through with water. Wash the filter, using as little water as possible.

Finally, wash the filter again with NH_4OH, then with water. Now add 80 c.c. of dilute H_2SO_4 (one volume to four of water) to the filtrate and then 10 grams of pulverized zinc.

The zinc should be fine enough to pass a 20-mesh sieve and must be as free as possible from iron. The very pure zinc now furnished for this process will sometimes act very slowly. To make it act promptly it should first be platinized as follows: Treat a quantity of the zinc with water, slightly acidulated with H_2SO_4 and containing a few drops of a solution of $PtCl_4$. After the reaction has proceeded a few minutes, pour off the liquid and wash the zinc thoroughly with water; dry it and preserve it in a glass-stoppered bottle. The almost infinitesimal trace of platinum precipitated on the zinc by this treatment causes the reaction to be rapid and powerfully reducing on the MoO_3.

Now warm till rapid effervescence ensues and heat gently 10 *minutes.* At the end of this time reduction will be complete.

Filter promptly through glass wool packed tightly in a funnel, and wash well with water. Care must be taken that no zinc passes through the mat of glass wool.

Now run the permanganate into the dark-colored filtrate until the color is discharged, and the last drop gives a faint pink tint, marking the end of the reaction.

There is always some impurity in the zinc, hence it is essential to make a *blank test,* using the 30 c.c. of NH_4OH, the 10 grams of zinc and 80 c.c. of sulfuric acid as before, but omitting the yellow precipitate. The filtrate in this test will always consume a small amount of permanganate, which must be determined and deducted from the amount taken in the regular determination, the difference being the permanganate solution equivalent to the yellow precipitate.

In working this process it is important to check it from time to time upon material similar to that to be analyzed, and in which the phosphorus has been determined gravimetrically.

Standardization of the Permanganate Solution.—The only strictly accurate method for the standardization of the permanganate is to use an iron or steel sample of known phosphorus content, such as the samples furnished by the U. S. Bureau of Standards or one which the analyst has carefully analyzed, using the gravimetric method, weighing the phosphorus as magnesium pyrophosphate.

Heat 1 liter of water to boiling and add dilute $KMnO_4$ until a faint pink appears. Cool to room temperature and dissolve 3.462 grams of pure permanganate in 500 c.c. of water, then dilute to a liter. Proceed with the determination of phosphorus in a standard sample as directed above. The amount of phosphorus in the sample used divided by the number of cubic centimeters of the permanganate solution used for titration gives the strength of the permanganate in terms of phosphorus. The standardization should be repeated at least three times.

Fairly accurate standardization of the permanganate can be secured by using the standardization results as obtained according to directions on page 37 for the standardization of permanganate against iron. The calculation is as follows: The 12 MoO_3 of the yellow precipitate when reduced by zinc theroretically becomes $6Mo_2O_3$, according to the reaction $12MoO_3 + 36H = 6Mo_2O_3 + 18H_2O$, but practical experience shows that only 34H is used in the reaction. As 34 atoms of hydrogen have a reducing power equivalent to that of 34 atoms of divalent iron, it will take the same amount of permanganate to oxidize one gram molecule of the reduced phosphomolybdate back to its original condition as will be required to oxidize 34 gram atoms of ferrous iron to ferric iron. Therefore, these relationships can be expressed mathematically as follows:

$P = (NH_4)_3PO_4.12MoO_3 = 34Fe$ and, consequently, the relationship betweeen the iron value of the permanganate and its phosphorus value is: phosphorus value = iron value $\times 31 \div 34 \times 55.84$ = iron value $\times 0.01634$.

To make a solution of such strength that 1 c.c. equals 0.01 per cent of phosphorus on a 1-gram sample, note that 2 molecules of permanganate will yield oxygen thus: $2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$. That is, 2 molecules of permanganate will give up 5 atoms of oxygen. Therefore, to yield 17 atoms of oxygen, which is the amount required to oxidize 1 molecule of the reduced yellow precipitate (equivalent to 1 atom of phosphorus) requires $17 \times 2/5$ or $6\,4/5$ molecules of $KMnO_4$. Therefore:

$$6\,4/5\,KMnO_4 : 1P. :: X : 0.0001,$$

or 1,074.6:31.04::X:0.0001. X equals 0.003462 gram $KMnO_4$ per cubic centimeter, or 3.462 grams per liter.

Titration of the Yellow Precipitate with Standard Alkali

This method is, in the writer's opinion, the best for steels or samples low in phosphorus. It is both rapid and accurate. It avoids the reduction and consequent uncertainty as to the oxide produced. The reaction may be written as follows:

$$12MoO_3, (NH_4)_3PO_4 + 23NaOH = 11Na_2MoO_4 + (NH_4)_2MoO_4 + Na(NH_4)HPO_4 + 11H_2O$$

Hundeshagen has shown that 23 molecules of NaOH are required to neutralize 1 molecule of yellow precipitate. This gives a ratio of 1 atom of phosphorus to 23 molecules of NaOH or, by weight 31, of P to 921.15 of NaOH, or 1:29.71. The alkali solution must be free from carbonate which would interfere with the end reaction. The best indicator is a dilute alcoholic solution of phenolphthalein. The alkali solution should be standardized against pure yellow precipitate carefully dried to constant weight at 150°C. As this substance is rather hygroscopic, it should be redried every time it is used. It is still better to standardize against a standard steel.

To prepare the yellow precipitate for standardizing, precipitate a dilute solution of Na_2HPO_4 by an excess of molybdic acid solution, first acidifying the phosphate solution with HNO_3. Wash the precipitate carefully with water and dry it as directed. Determine the phosphorus in a portion of it gravimetrically. It should contain 1.63 per cent of phosphorus.

Process of Analysis.—Wash the precipitate of phosphomolybdate obtained as directed on page 55 with a 2 per cent solution of HNO_3 until the iron stain is removed from the filter paper, then with a 2 per cent solution of KNO_3 until the washing does not turn blue litmus paper red. Put the filter containing the precipitate back into the flask in which the precipitation was made, and add to the flask and its contents a measured quantity, usually 10 or 20 c.c. of standard NaOH. Dilute to 50 c.c. with CO_2 free water, add 2 drops of phenolphthalein; shake to disintegrate the filter and dissolve the precipitate, and then titrate the excess of alkali with standard acid. Finally, add standard alkali until the pink just reappears. The difference between the number of cubic centimeters of nitric acid equivalent to the soda solution used and that required in the titration will be the nitric acid equivalent to the phosphorus; and if the nitric acid is of correct strength, each cubic centimeter will represent 0.01 per cent of phosphorus.

In dissolving yellow precipitate by standard alkali, always keep the liquid cool and the solutions dilute, as ammonia is set free in the reaction and is liable to be lost by volatilization if the liquid is concentrated. This would cause error in the nitric acid titration.

References on the Titration Method:

J. Anal. App. Chem., **6**, 82.
J. Anal. App. Chem., **6**, 204.
J. Anal. App. Chem., **6**, 242
Z. anal. Chem., **28**, 171.
Stahl u. Eisen, **26**, 297.
"Methods of the U. S. Steel Corporation."

Preparation of the Solutions. Standard Sodium Hydroxide and Standard Nitric Acid.—One-tenth normal solutions may be used. In this case 1 c.c. NaOH is equal to 0.000135 gram phosphorus.

It is more convenient to have a solution of such a strength that 1 c.c. equals 0.0002 gram phosphorus; then, if 2 grams of steel are taken for the analysis, each cubic centimeter of hydroxide solution will be equivalent to 0.01 per cent of phosphorus. To make such a solution, proceed as follows:

Dissolve 15.4 grams of NaOH as free as possible from Na_2CO_3 in about 200 c.c. of water. Now add a saturated solution of $Ba(OH)_2$ as long as a precipitate forms. Filter at once from the $BaCO_3$ and dilute to 2 liters. This solution will be a little too strong. Now prepare an approximate HNO_3 solution by diluting 20 c.c. of concentrated HNO_3 to 2 liters. Fill a burette with this acid and titrate it carefully against 10 c.c. of the NaOH solution. Next weigh 0.1226 gram of dry yellow precipitate (equal to 0.002 gram of P) into a beaker; add 50 c.c. of water and 10 c.c. of the NaOH solution, which should dissolve the precipitate to a perfectly clear solution. Add 3 drops of phenolphthalein solution and titrate with the acid till the color vanishes. Finally, add standard NaOH until the pink just reappears. The difference between the acid required for the NaOH and that required in the second case is the number of cubic centimeters of the HNO_3 equivalent to 0.002 gram of phosphorus. Now add sufficient water to the dilute nitric acid to make 10 c.c. exactly equal to 0.002 gram of phosphorus. Repeat the test with the yellow precipitate and soda solution, using double the amount of yellow precipitate and 30 c.c. of soda. If the nitric acid is not exactly right, correct it by further dilution and repeat the test.

Finally, dilute the soda solution until it is exactly equivalent to the nitric acid.

As a check, the HNO_3 should also be standardized against pure sodium carbonate (Na_2CO_3). Proceed as follows: Put 5 grams of the pure salt in a platinum crucible, cover the crucible with a lid and embed the crucible nearly to the top in a sand-bath and place a thermometer in the sand by the side of the crucible. Heat the sand-bath until the temperature rises to 270 to 300°C., and keep it at that temperature for a half hour. This is to drive out all moisture without decomposing the carbonate. Cool the crucible and contents in a desiccator. Weigh out 0.212 gram of the carbonate, dissolve in 20 c.c. of distilled water, add a few drops of methyl orange indicator and titrate with the nitric acid solution until its color becomes distinctly red when compared with the color of another solution of the same volume containing the same amount of methyl orange and a little sodium carbonate. If the nitric acid is exactly N/10, just 40 c.c. should be required for the titration.

The nitric acid, if preserved in a tightly stoppered bottle, keeps its standard indefinitely, but the soda solution will slowly change on account of absorption of CO_2 by the slight excess of $Ba(OH)_2$ present and must be retested against the acid frequently. This can be prevented by using a guard tube containing soda lime. The soda solution also changes strength by attacking the glass. This is avoided by paraffining the inside of the bottle.

In standardizing the acid and alkali, instead of taking yellow precipitate directly, a sample of steel of known phosphorus content may be weighed out and treated as in the regular process. It is well to check the solution finally in this way in all cases.

Phenolphthalein Solution.—Dissolve 0.2 gram of the indicator in 200 c.c. of 95 per cent alcohol.

Methyl Orange Solution.—Dissolve 0.025 gram of the sodium salt in 100 c.c. of water and add 0.70 c.c. of N/10 HCl.

THE DETERMINATION OF PHOSPHORUS IN FERRO-ALLOYS AND ALLOY STEELS

These alloys present some difficulties in the determination of phosphorus for two reasons: The alloy may dissolve with difficulty and leave an insoluble residue, and the alloying element may interfere with the complete and pure precipitation of the phosphomolybdate.

The only steels which require special treatment for solution are those which leave a residue at any time during the treament, such as certain chrome steels, steel containing a high percentage of silicon, titánium or zirconium and tungsten steel.

The preliminary solution of chrome steel should be as in plain carbon steel, except that the nitric acid treatment must be continued until all carbides are in solution, a few drops of sulfuric acid being added if necessary.

With steel containing a high percentage of silicon, the preliminary solution is carried on as usual, except that the HNO_3 solution should be evaporated to dryness with HCl to remove SiO_2, then treated as for ores on page 49.

Steels containing much titanium or zirconium are apt to cause difficulties, owing to the separation of titanium or zirconium phosphates. In case these are in evidence after the final digestion in HNO_3, the solution should be diluted with hot water, digested for a longer period, filtered and the residue washed, ignited, fused with sodium carbonate, and the water extract of the melt added to the main solution.

Tungsten steel does not dissolve in nitric acid, and is treated as follows:

Dissolve 1 to 3 grams of the sample in a porcelain dish provided with a cover glass, with 20 c.c. of nitric acid (sp. gr. 1.42) and 60 c.c. of hydrochloric acid (sp. gr. 1.19). Heat gently until the sample is decomposed and then evaporate to dryness. Remove the cover glass and bake until the acid is completely expelled. Cool, add 30 c.c. of hydrochloric acid (sp. gr. 1.19) and warm until the soluble salts are dissolved. Dilute to 100 c.c., filter, wash with dilute hydrochloric acid (1:10) and evaporate the filtrate to syrupy consistency. In the meantime dissolve the tungstic acid on the paper in hot, dilute ammonium hydroxide, washing the paper first with hot, dilute ammonium hydroxide, then with hot, dilute hydrochloric acid. Render the solution faintly acid, add 1 gram of alum, and then ammonium hydroxide in slight excess. Boil for three minutes, filter, wash slightly with hot water containing a little ammonium chloride and discard the filtrate. Dissolve the precipitate in hot, dilute hydrochloric acid, add the solution to the main solution which is being evaporated and proceed as directed for iron ores on page 50.

Vanadium steel offers no difficulty in solution but makes necessary some precautions during the precipitation of phosphomolybdate. Johnson has shown that the only precaution necessary is to have a solution containing 40 to 50 per cent by volume of strong nitric acid (sp. gr. 1.42) when the molybdate solution is added to precipitate the phosphorus, otherwise analyzing for phosphorus exactly as described on page 55 for steels. Indeed, it is always safest to use this procedure, since so many steels contain some vanadium. The errors resulting from the presence of vanadium may also be avoided if the vanadium is reduced from the pentavalent to the quadrivalent state just before the molybdate solution is added. To do this proceed as directed on page 55, cool to 20°C., add N/10 ferrous sulfate until the vanadium color is discharged, then proceed as usual for the precipitation of phosphorus, except that the solution is kept cold and given a much longer time for the precipitate to settle.

Ferro-alloys present more difficulties than the alloy steels, both because of difficulties of solution and the presence of large amounts of interfering elements. In all cases it is best to use 0.5-gram samples. The ferro should be pulverized as finely as possible before weighing.

Dissolve ferromanganese in nitric acid, evaporate to dryness and bake over the full heat of a Bunsen burner until the acid is completely expelled, then treat exactly as directed for iron ores.

Dissolve spiegel and silico-spiegel in a mixture of 20 c.c. of HCl and 25 c.c. of 1:1 HNO_3, evaporate to dryness and bake and then treat as for iron ores.

Treat ferrosilicon the same as silico-spiegel, except that the solution should be made in a large platinum crucible or dish, adding HF occasionally until the solution is complete. Add 5 c.c. of sulfuric acid and evaporate until fumes of SO_3 appear and *all HF is expelled.* Transfer to a beaker, neutralize with ammonia, make acid with nitric acid and proceed as usual.

Dissolve ferrovanadium in 30 c.c. of HCl and 30 c.c. of HNO_3, add 100 c.c. of HNO_3 (strong), evaporate to dryness and bake intensely for several minutes. Dissolve in 35 c.c. HCl, evaporate to 10 c.c., add 50 c.c. HNO_3, evaporate to 10 c.c. and add

10 c.c. more of HNO_3. Heat and filter through an asbestos mat in a Gooch crucible. Wash the brick-red V_2O_5 with strong nitric acid containing 2 per cent of phosphorus-free $Fe(NO_3)_3$. Evaporate the filtrate to 10 c.c. and again filter off V_2O_5. Evaporate to 10 c.c. a third time and filter if V_2O_5 appears. The vanadium is now reduced to so low a figure that the solution can be treated as directed for vanadium steels.

Fuse ferrotitanium in a platinum crucible with 10 grams of sodium carbonate and 1 gram of sodium nitrate, disintegrate the cake by digestion with hot water until no hard particles remain. Filter, wash with water, ignite the paper and sodium titanate and again fuse with a small amount of sodium carbonate, disintegrate with water, filter and wash. The titanium remains on the filter as sodium titanate while the phosphorus is in the filtrate. Make the combined filtrates acid with HCl, evaporate to dryness, dissolve in dilute HCl, filter off the silica and proceed as usual.

Fuse ferrochrome with 10 grams of sodium peroxide in a nickel crucible lined with sodium carbonate. The temperature is maintained below the melting temperature of the carbonate. Cool, disintegrate the cake with hot water until no hard particles remain, boil for five minutes to decompose the peroxide, make acid with dilute H_2SO_4 and then alkaline with ammonia. The phosphorus precipitates as ferric phosphate with the ferric hydroxide. Filter, wash well with hot water, dissolve in HCl, evaporate to dryness and proceed as usual.

Dissolve ferromolybdenum in a platinum dish with 20 c.c. of HNO_3 1:1. When the reaction ceases add 20 c.c. of 1:1 H_2SO_4 and a few drops of HF and evaporate until fumes of SO_3 appear. Add 30 c.c. of water, heat and filter off any WO_3 present. Add ammonia until slightly alkaline, evaporate if necessary to 50 c.c., add 50 c.c. of strong HNO_3 and precipitate as usual.

Dissolve ferrotungsten with 10 c.c. of strong nitric acid in a platinum dish, add HF a few drops at a time until the solution is complete, add 10 c.c. of 1:1 H_2SO_4, evaporate until SO_3 fumes heavily, cool, add 50 c.c. of 1:1 HCl, heat for a half hour, filter off the WO_3, evaporate to 10 c.c. and proceed as usual.

REFERENCES:

JOHNSTON, *Ind. Eng. Chem.*, **11**, 113.

U. S. Steel Corporation, "Methods for Analysis of Ferro-alloys."

CHAPTER V

THE DETERMINATION OF SILICON IN IRON

The metals in which silicon has most frequently to be determined are pig iron, containing from ½ to 4 or 5 per cent; "ferrosilicon," containing up to 30 per cent, steel with from traces to 1 per cent; and wrought iron with small fractions of 1 per cent.

In all these the silicon is combined as FeSi, not as SiO_2, though there may be a little SiO_2 included as intermixed slag, especially in wrought iron.

All of these metals are soluble in HNO_3 (sp. gr. 1.2) except ferrosilicon, the silicon being oxidized to SiO_2, which passes wholly or in part into solution. Evaporation of the HNO_3 solution to dryness, baking and re-solution in HCl renders this SiO_2 only partially insoluble, a temperature of 250°C. not causing all the SiO_2 to separate. The evaporation to dryness breaks up any soluble H_2SiO_3 forming insoluble SiO_2.

To accomplish the complete separation of the silica by this means it is necessary to evaporate to dryness, bake as in the phosphorus determination, dissolve in HCl, filter and again *evaporate to complete dryness*, expelling all the HCl. On taking up again in HCl, practically all of the silica is left insoluble. After dilution the solution may be filtered from the residue of silica + carbon, which after thorough washing, first with HCl and then with water, may be ignited till the carbon is burned off, and weighed.

The silica thus obtained is rarely pure, and must be treated with H_2SO_4 and HF, or must be fused and the silica separated from the fusion. (See analysis of clays.)

Hydrochloric acid or aqua regia may be used to dissolve the metal instead of HNO_3, but they do not attack ordinary iron so rapidly. Finally, solution in H_2SO_4 and HNO_3 and evaporation till fumes of H_2SO_4 are given off will cause a complete separation of the silica.

REFERENCES:

For details of these various methods see—

BLAIR, "Chemical Analysis of Iron" (nitric acid method).

TROILIUS, "Notes on the Chemistry of Iron," p. 35 (sulfuric acid method).

Also *Trans.* Am. Inst. Min. Eng., **10**, 162, *et seq.*, and 187, *et seq.*

When a nitric or hydrochloric acid solution containing silica is evaporated with H_2SO_4 the volatile acids will be expelled, and if the temperature is finally raised to near the boiling point of the concentrated acid, the silica is completely dehydrated and becomes insoluble. Titanic acid, if present, passes into solution and the silica thus obtained is pure. The following method, slightly modified from one published by Dr. Drown, depends upon this fact. (*Trans.* Am. Inst. Min. Eng., **7**, 346.)

Process for Pig Iron and Steel.—Weigh out 0.9386 gram of pig iron or 4.693 grams of wrought iron or steel. Put into a casserole or dish and cover with a large watch-glass. Add carefully 30 c.c. of a cold mixture of 8 parts by volume of concentrated HNO_3, 5 parts of concentrated H_2SO_4 and 17 parts of H_2O (for the pig iron), or 100 c.c. of a mixture of 35 parts of concentrated HNO_3, 15 parts of H_2SO_4 and 50 parts of H_2O (for the steel), or use the three-acid mixture given further on.

Warm till action ceases, then boil down rapidly on an iron plate or over the bare flame until the $Fe_2(SO_4)_3$ separates as a white mass; continue the heating until dense fumes of sulfuric acid are evolved. These have a peculiar suffocating odor, easily recognized. Their formation indicates the total expulsion of the HNO_3, and this is absolutely necessary in order to make the silica insoluble. In the case of steel low in silicon it is necessary to stir up the mass of ferric sulfate thoroughly or it may include silica not dehydrated and so cause loss (DUDLEY). There will be danger of "spattering" unless the heating is carefully done, but if the dish is well covered, this need cause no loss.

Now let cool, then add 10 c.c. of concentrated HCl and wash off the cover into the dish. Dilute to 150 or 200 c.c., cover, set over a burner and boil until all $Fe_2(SO_4)_3$ is dissolved. This can be recognized by the disappearance of the silky precipitate in the liquid. Continue the boiling for five minutes, as this will cause the solution to filter more easily. Then wash off the cover, and let the liquid stand until all the silica settles. Decant the clear liquid through a 7-cm. ashless filter, previously washed out with boiling water. Finally, transfer and wash the residue with hot water. When partially washed, drop a little HCl on the filter and residue, then wash again with hot water till the filtrate no longer tastes acid. Without drying, transfer the filter to a crucible and ignite, gently at first, finally at high heat, until all the carbon (graphite) is burned and the silica is white. If this is done in a platinum crucible and over a blast lamp the burning off of the carbon need not take more than a few minutes.

It is important that the temperature be low at first, not exceeding a dull red until the paper and the amorphous carbon are burned out, as overheating at first will cause the carbon to lump together and it will then burn very slowly. During the final heating over the blast lamp keep the crucible partly covered. The burning may be hastened by directing a gentle current of oxygen gas into the crucible, but if due care is taken this is not necessary. If oxygen is used take care not to blow any particles of silica out of the crucible by forcing in the gas too rapidly.

The weight of the silica in milligrams divided by 2 in the first case or by 10 in the second gives the silicon in tenths of a per cent.

Notes on the Process.—If the above directions are followed exactly as to the dilution and boiling of the solution there will be no need of a filter pump to secure rapid filtration. Boiling with a large excess of water consolidates the silica so that it filters easily. The funnels and filter paper should be carefully selected; the former should have long and narrow stems that will fill with the liquid and produce a little suction. The funnel angle should be 60 deg. A porous ashless paper like the Muncktel "black label" is desirable. The precipitate of silica has no tendency to run through, so that a dense paper is not necessary.

The filter should be kept full while filtering the solution as, if it is allowed to empty, the paper will become clogged.

For pig iron and ferrosilicons, the following three-acid silicon mixture may be substituted for that already given, and will be found very efficient:

Water	150 c.c.
Sulfuric acid, sp. gr. 1.84	40 c.c.
Nitric acid, sp. gr. 1.42	80 c.c.
Hydrochloric acid, sp. gr. 1.19	60 c.c.

Mix in the order given and preserve for use. Of this mixture 25 c.c. are enough for the "factor weight" of pig iron (0.4693 gram). Evaporate to strong fumes of H_2SO_4, cool, add a little concentrated HCl, then add water and boil. With this mixture the silica filters particularly well. With steel where the silicon is in very small amount it is necessary to test its purity. Add a drop of H_2SO_4 to the silica in the crucible and then a few drops of pure HF or a few crystals of NH_4F. Evaporate to dryness over a low flame, not allowing the liquid to boil, and ignite the residue strongly. The fumes of HF are poisonous, so the evaporation must be made under a good hood. The silica passes off as volatile SiF_4. If any residue remains, weigh it and deduct it from the total weight. The difference is SiO_2.

The following process is sometimes used for furnace control instead of the one just given.

The molten iron is chilled by pouring into water. This makes it very brittle. It is then pulverized in a steel mortar, dissolved in HCl, rapidly evaporated to dryness, taken up in HCl, diluted and filtered. Without drying, the filter is put into a platinum crucible, ignited in a steam of oxygen and weighed. The time required for this process is said to be 12 minutes.

In preparing the drillings for analysis, great care must be taken to keep them free from sand. This is difficult in the case of pig iron, drillings from which should usually be cleaned.

This is easily accomplished by folding a sheet of paper over a magnet, then picking up the metal against the paper. The sand and other foreign particles are left behind. On drawing the magnet away from the paper, the drillings will fall off and can be collected on a clean sheet of paper. All the drillings must be gone over and no considerable residue should remain. If much graphite-like substance is separated, it may hold silicon belonging to the sample.

The drillings should be fine. Large fragments of metal dissolve slowly and may be left as hard grains in the silica, of course vitiating the result. If these lumps remain, add more acid and heat slowly until they dissolve.

Ferrosilicons may need to be pulverized till they go through bolting cloth before they will dissolve.

In weighing out, great care must be taken to secure an average of fine and coarse, as these usually differ in percentage of silicon.

To avoid unnecessary calculation, it is usually convenient to weigh out the "factor weight" of the metal. SiO_2 contains 0.4693 Si; hence, if that weight in grams is taken for the analysis, each milligram of silica will indicate $\frac{1}{10}$ per cent. In low silicon irons or steel, 0.9386, or some other multiple of the factor, may be used.

Determination of Silicon in Ferrosilicon.—This material is not easily attacked by any of the above mixtures. If not too high in silicon, it can usually be dissolved by prolonged boiling with aqua regia, adding fresh acid from time to time. Finally, add 25 c.c. of dilute (1:3) H_2SO_4, evaporate until fumes of sulfuric acid appear, and then finish as in the regular process.

Samples with over 10 per cent silicon and which aqua regia will not dissolve are, according to Williams, best treated by fusing with six or eight times their weight of dry Na_2CO_3. Then proceed with the fusion, as in the determination of silica in a limestone. The metal must be very finely pulverized and not more than 0.5 gram taken. (WILLIAMS, *Trans.* Am. Inst. Min. Eng., **17**, 542.) See directions for ferrotitanium on page 65.

Instead of Na_2CO_3 alone, a mixture of Na_2CO_3 and $NaNO_3$ or Na_2O_2 may be used and the fusion conducted as described on pages 105, 136. But these reagents are much more injurious to the platinum than the carbonate, though more fusible and more rapid in their action. A nickel crucible may be used with Na_2O_2.

Determination of Silica in Admixed Slag in Steel.—It is sometimes necessary to distinguish between the silicon combined in the steel as silicide and that combined as admixed slag. The following method depends upon the fact that iron is dissolved with iodine, while slag is unattacked. Silica formed from the silicide is soluble in caustic soda.

Process.—Place 5 grams of the drillings in a beaker, put the beaker in a dish filled with ice or snow and pour over the drillings 25 c.c. of ice-cold water. Add gradually about 30 grams of resublimed iodine, stirring until the iodine is all dissolved. Keep the beaker covered with a glass and constantly surrounded with the scraped ice or snow. Stir the solution frequently, until the iron is all dissolved. Then add 100 c.c. of cold water; allow the insoluble matter to settle and decant the liquid through a small filter. Wash the insoluble residue several times with water by decantation. If any metallic iron remains, give the residue a further treatment with iodine. Transfer the insoluble matter to the filter, wash once with 1:20 HCl, then wash well with water a dozen times. Wash the residue on the paper back into a platinum dish, add enough NaOH to make a 10 per cent solution and heat to boiling for several minutes. This dissolves any precipitated silica formed from the silicide of the steel. Decant the liquid through a small filter, and again boil the insoluble matter with 50 c.c. of 10 per cent NaOH solution. Filter this through the same paper, wash several times with hot water and, finally, wash with dilute HCl (1:20) and again several times with hot water. Ignite and weigh as slag and oxide. In *this then* determine the silica as in a steel.

Silicon in Other Ferro-alloys.—Determine silicon in ferromanganese as directed for spiegel, in electroferrosilicon by the fusion method, using sodium peroxide in a nickel crucible. In ferrotitanium proceed as directed for spiegel, always finishing with the treatment of the silica precipitate, since it will contain a large HF amount of TiO_2. Dissolve ferrochromium in dilute H_2SO_4 and evaporate to fumes of H_2SO_4, dissolve in water and filter, fuse the residue with sodium carbonate, dissolve in water, acidify with H_2SO_4, evaporate to fumes and proceed as usual. Fuse ferrovanadium in a platinum crucible with 6 grams of sodium carbonate and ½ gram of sodium nitrate, dissolve in water, acidify with H_2SO_4, evaporate and proceed as usual. Ferrovanadium low in silicon is soluble in acids and need not be fused. Ferromolybdenum is soluble in nitric acid also and is analyzed as ferromanganese. Fuse ferrotungsten with sodium peroxide in a nickel crucible, keeping it molten for five to ten minutes, dissolve in hot water, acidify with H_2SO_4, add 10 c.c. of phosphoric acid (sp. gr. 1.72), evaporate to fumes of H_2SO_4, dissolve in dilute HCl, filter, wash, ignite and weigh the impure SiO_2, then purify with HF as usual.

REFERENCE:

U. S. Steel Corporation, "Methods for Analysis of Ferro-alloys."

CHAPTER VI

THE DETERMINATION OF MANGANESE

There are two classes of material to be considered: first, ores, slags and metals high in manganese, such as manganite and ferromanganese containing from 15 to 90 per cent; second, ordinary iron ores, pig irons and steel, containing from a trace up to about 3 per cent of manganese. These call for a somewhat different treatment.

Manganese is present in ores chiefly as the minerals pyrolusite (MnO_2), magnanite ($MnO(OH)$) and other oxide minerals containing Mn_2O_3 and Mn_3O_4, the carbonate, rhodochrosite, the silicate, rhodonite, and other less important minerals. In iron and steel the manganese is present partly as the sulfide (MnS) and the carbide (Mn_3C); the rest of the manganese is in solid solution in the iron. Manganese is added intentionally in steel making to decrease the evil effects of sulfur by forming MnS, to deoxidize the iron forming MnO which goes chiefly into the slag and, in addition, the manganese greatly effects the properties of iron by its effect on critical temperatures.

Manganese may be determined by either the gravimetric or volumetric methods. When gravimetric methods are used the manganese is separated from ron and other elements by taking advantage of the fact that MnO_2 is insoluble in nitric acid; or the iron and other common metals, such as aluminium and titanium, are separated from the manganese by precipitating them by hydrolysis, the manganese remaining in solution. The manganese may be finally precipitated as manganese ammonium phosphate.

Volumetric methods depend upon the fact that manganese may exist in solution in the di-, tetra-, and heptavalent conditions. When proper conditions in solution prevail it is possible accurately to measure the amount of manganese in solution by measuring the amount of standard reagent required to change the manganese from one condition of valence to another.

THE BASIC ACETATE PROCESS

This process is widely used as a standard method, especially in rock analysis. It depends upon the precipitation of ferric iron, aluminium, titanium and zirconium by hydrolysis in slightly acid solution, thus separating these elements from manganese. The separation is satisfactory only under carefully controlled conditions, hence the process must be operated very precisely as to details.

When ammonium hydroxide is added to a hydrochloric acid solution of iron ore until the acidity is reduced to a very low value, the solution becomes very dark red in color, owing to the formation of a basic chloride of iron, the iron remaining unprecipitated even when the relationship corresponds to one part of ferric chloride to ten parts of ferric hydroxide, although the solution still reacts acid to litmus. If sodium or ammonium acetate is added to this solution the acidity is still further reduced, owing to the mass action effect of the large concentration of acetate ion upon the very weakly dissociated basic acetate of iron which hydrolizes thus. $Fe_x(C_2H_3O_2)_y(OH)_z + yHOH = xFe(OH)_3 + yHC_2H_3O_2 + zH_2O$. The acetic acid liberated by the hydrolysis has its hydrogen ion concentration so reduced by the mass effect of the acetate present that the precipitation of the ferric hydroxide and aluminium hydroxide goes to completion. Under these circumstances the manganese does not precipitate nor do nickel, zinc, cobalt and copper. The separation is not entirely perfect, hence for the best results a double precipitation must be made.

It has been shown by Lundell and Knowles that the separation of manganese and nickel from iron and aluminium, when the latter are present in moderate amounts, can be satisfactorily carried out by the use of ammonia under closely controlled conditions.

THE ACETATE PROCESS FOR ORES LOW IN MANGANESE

In this case it is desirable to work upon large amounts of material. The filtration and washing of a large basic acetate precipitate is very troublesome, and can be avoided by taking an aliquot part of the solution after the precipitate has settled. The error introduced by neglecting the volume of the precipitate is inappreciable when the percentage of manganese is small.

A single precipitation of the iron is entirely sufficient, provided care be taken to avoid excess of sodium acetate.

Extreme care in measuring the solution, as well as in keeping the temperature constant, is also superfluous when less than 3 per cent of manganese is present and the volumes are kept large; 10 c.c. on a liter causing an error of only 0.03 per cent.

The precipitate by bromine is MnO_2. On ignition at moderate temperatures with ample access of air, it changes principally to Mn_3O_4, though the exact nature of the oxide produced varies with the conditions of heating. This precipitate also usually retains small amounts of sodium salts. For these reasons the percentage of manganese which it contains is always a little uncertain. As the variations are limited to a small percentage of the weight of the precipitate, the results obtained by weighing it directly will be sufficiently accurate for all ordinary work, where but little manganese is present. The method separates Fe, Ti, Zr and V from Mn, Ni, Cu, Zn.

Process of Analysis.—Dissolve 4 grams of the ore in 30 c.c. concentrated HCl exactly as in the iron assay. If there is any ferrous iron present, add about 1 cc. of HNO_3 to convert it completely to ferric chloride. Boil the solution until the excess of HNO_3 is decomposed and the chlorine expelled. The evaporation need not go so far that insoluble iron salts separate; should such form, add more HCl and heat until they dissolve. Add water, warm and filter from the residue.

Take a large Erlenmeyer flask, one which will hold when quite full 2,400 c.c. Dry it, then measure into it exactly 2,000 c.c. of water; this should reach up into the narrower portion of the flask. Paste a thin strip of paper on the glass to indicate exactly the level of the liquid. The flask must be set on a level desk, and the place it stands on as well as the position of the paper mark noted, so that it can be subsequently returned *to the same position.*

Now transfer the solution of the ore to the flask, and dilute it to about 1,700 c.c. Then add a saturated solution of Na_2CO_3 gradually until the liquid begins to grow dark red. Continue to add the reagent drop by drop, shaking the flask after each addition until the liquid is very dark in color and the precipitate formed redissolves very slowly. The object is to reach a point just short of that at which the iron is precipitated. The operation requires practice. Should the point be overstepped, add a little HCl, and when the liquid becomes clear, neutralize again; but in this case, in the writer's opinion, the iron precipitate is more likely to contain manganese.

Now add 6 grams of pure sodium acetate. Set the flask on a hot plate and boil the solution vigorously.

The iron should immediately separate as a bulky, red precipitate. If it fails to do so at once, drop in very cautiously a dilute solution of ammonia until the separation is complete. Now boil a few minutes longer, then remove the flask to the place where it stood when it was graduated, placing it in the same position, and fill it exactly to the mark with cold water. Stir the liquid thoroughly with a long rod, then let it settle. As soon as it is clear pour off 1 liter into a graduated flask. This whole operation can be done so quickly that the liquid will not cool materially.

Filter the measured portion of the liquid. The filtrate should be colorless and distinctly acid to litmus paper.

Concentrate the filtrate to about 500 c.c. Add 5 grams of sodium acetate and boil. Should any precipitate form, filter it off, dissolve it in HCl containing a little oxalic acid and add ammonia until methyl red just turns yellow. Boil this liquid, filter from any precipitate and add the filtrate to the main solution.

Finally, add bromine water, warm until the MnO_2 settles completely, filter, wash well with hot water, ignite and weigh as Mn_3O_4 containing 0.7203 Mn. Calculate the result on 2 grams of ore taken. The Br precipitates the Mn through the reaction $2Br+MnCl_2+2H_2O=MnO_2+2HCl+2HBr$.

Should the ore leave but little residue, this need not be filtered off, but may go into the flask with the solution. In applying, this process to slags and ores containing decomposable silicates, the HCl solution must be evaporated to dryness, taken up again in HCl, HNO_3 added and boiled off as usual.

If the ore contains large amounts of Ca, Mg, Zn, etc., the precipitate will be contaminated with manganites of these metals. The precipitate should be dissolved in HCl, made alkaline with ammonia, H_2S added, the MnS filtered, washed, ignited, converted to $MnSO_4$ with H_3SO_4 ignited to 500°C. and weighed as $MnSO_4$, which is very accurate.

The ferric precipitate obtained as above will always carry with it a small amount of manganese which can be separated by dissolving in hydrochloric acid and making a second precipitation. A better way, however, is to dissolve the hydroxides in sulfuric acid, evaporate to fumes of SO_3, dissolve in water and determine the manganese as directed under the bismuthate-arsenite method.

The acetate process can be applied to pig iron and steel but is seldom necessary or advisable.

Separation by Ammonia.—Dissolve the ore as directed for the acetate process, add enough HCl to make 5 grams of ammonium chloride per 200 c.c. of solution, add 10 drops of a 2 per cent alcoholic solution of methyl red, dilute to 250 c.c. per gram of sample used, heat to boiling and add dilute ammonium hydroxide until the color just changes to a distinct yellow. Boil two minutes more, filter and wash with hot 2 per cent ammonium chloride solution. Dissolve the precipitate and repeat the precipitation. In the filtrate precipitate the manganese with bromine as under the acetate process. Filter, wash the manganese dioxide with hot water, ignite and weigh as Mn_3O_4. This process is satisfactory in the absence of nickel and cobalt. The MnO_2 may be evaporated with H_2SO_4, heated to 500°C. and weighed as $MnSO_4$.

Should the ore contain nickel or cobalt, these will contaminate the manganese precipitate and the results will be inaccurate. In this case the precipitate of MnO_2 must be redissolved in HCl containing a little sodium sulfite. The solution is boiled until free from SO_2, then cooled and nearly neutralized by Na_2CO_3, a little sodium acetate added and the nickel and cobalt precipitated by H_2S. In the filtrate from these sulfides the manganese can be determined either by precipitation with bromine or as phosphate.

REFERENCE:

BLUM, *J. Am. Chem. Soc.* (1916), 2, 12.

CHLORATE METHOD FOR MANGANESE

When potassium or sodium chlorate is added to a solution of manganese in hot concentrated HNO_3, the manganese is all precipitated as MnO_2. To secure complete and rapid precipitation the chlorate should be added to the boiling solution in successive small portions, the HNO_3 must be in large excess and concentrated, HCl must be absent and there must be at least as much iron as manganese in the solution. The precipitate may be filtered off on an asbestos filter and washed with concentrated HNO_3. MnO_2 is entirely insoluble in cold concentrated HNO_3, provided this contains no lower oxides of nitrogen ("red fumes"); if these are present, that is, if the HNO_3 is not *perfectly colorless*, the MnO_2 will be reduced and dissolved.

After washing, the precipitate may be redissolved and the manganese determined gravimetrically as pyrophosphate or sulfate or volumetrically by measuring the oxidizing power of the MnO_2 on ferrous sulfate or oxalic acid, or hydrogen peroxide.

The reactions of the chlorate are:

$$2KClO_3 + 2HNO_3 = 2KNO_3 + H_2O + Cl_2 + 5O.$$
$$5Mn(NO_3)_2 + 5O + 5H_2O = 5MnO_2 + 10HNO_3.$$

The precipitate contains a little iron but is free from other impurities. When the solution to which the chlorate is added contains any HCl, this is first acted upon and broken up before the MnO_2 will separate, chlorine being driven off and water formed by the oxidation. This will result in weakening the HNO_3, and hence, in this case, more HNO_3 must be present to prevent too great loss of strength.

The method is especially adapted to the determination of manganese in steels and irons low in silicon and dissolving in HNO_3 without residue. If SiO_2 is present in the solution, it may separate in a gelatinous form which prevents filtration and coats the particles of the precipitate so that they dissolve with difficulty. It should be removed by the addition of a few drops of hydrofluoric acid to the liquid after the precipitation of the MnO_2. Sodium chlorate is preferable to potassium chlorate because its greater solubility makes it easier to wash out of the precipitate.

Process for Steel Low in Silicon.—Dissolve 5 grams in 60 c.c. HNO_3 (1.2 sp. gr.) in a 200-c.c. beaker. Evaporate to 25 c.c., then add 100 c.c. of *colorless concentrated* HNO_3. Set on an iron plate and heat to incipient boiling. Now drop in powdered $NaClO_3$ or $KClO_3$, a little at a time, adding each portion when the effervescence produced by the preceding portion has ceased. By the time 2 to 2½ grams have been added the MnO_2 will have separated as a fine brown powder. Now add ½ gram more of the chlorate and boil gently for 10 minutes. If any SiO_2 is present in the solution after three or four minutes boiling, add a few drops of pure HF. Then add 1 gram more of the chlorate and 25 c.c. concentrated HNO_3 and boil 10 minutes longer. Remove from the plate and cool by setting the beaker in water. When the MnO_2 has settled, filter without dilution, through an asbestos filter in a Gooch crucible. Finally, transfer the MnO_2 to the filter and wash beaker and filter with *colorless concentrated* HNO_3, three or four times, or until the filtrate is colorless. This can be done without using more than 15 or 20 c.c., adding only a little each time and letting each portion run through before adding the next. Finally, wash with a little cold water. If the HNO_3 is colored by lower oxides of nitrogen (from standing and the action of light), it can be purified by blowing a strong current of air through it until it becomes colorless.

After washing the MnO_2 with cold water till the acid taste is gone from the filtrate (letting each successive portion of water run entirely through before adding the next, so as to not use in all more than 20 c.c.), wash the asbestos and precipitate back into the beaker (which always has some MnO_2 adhering to it).

Volumetric Determination of the Mn.—This process consists in dissolving the MnO_2 in a measured excess of an acid solution of ferrous sulfate of a known strength. Each molecule of MnO_2 changes two molecules of ferrous sulfate to ferric sulfate. The amount of ferrous sulfate remaining is then determined by a standard solution of potassium permanganate. The reactions are as follows:

1. $MnO_2 + 2FeSO_4 + 2H_2SO_4 = MnSO_4 + Fe_2(SO_4)_3 + 2H_2O.$
2. $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$

The process requires, first, a solution of potassium permanganate of a known strength; second, a solution of ferrous sulfate in dilute sulfuric acid. The strength of this is determined by titration with the permanganate solution.

Preparation of the Permanganate Solution.—Dissolve 1.151 gram of pure $KMnO_4$ in water and dilute to 1 liter. One cubic centimeter of this solution will have the same oxidizing power as 0.001 gram of manganese in the form of the brown precipitate (MnO_2). Check the solution against pure iron or pure ammonium ferrous sulfate, $(NH_4)_2Fe(SO_4)_26H_2O$, in exactly the same way as directed for the standardization of $KMnO_4$ on page 37. A better way is to use a standard ore.

Preparation of the Ferrous Sulfate Solution.—Dissolve 20.18 grams of pure crystallized ferrous sulfate ($FeSO_47H_2O$) in about 500 c.c. of water, to which 25 c.c. of concentrated H_2SO_4 has been added, and then dilute to 1 liter.

Determine its strength against the permanganate solution by measuring 15 c.c. with a pipette into a beaker, adding about 25 c.c. of water and 1 c.c. of H_2SO_4 and then running in the permanganate till the pink color is permanent. About 30 c.c. should be required. This value must be determined frequently as the solution of ferrous sulfate alters rapidly from the oxidizing action of the air. In large amounts it is best kept in a carboy with some aluminium wire. The solution can be preserved in this way for some time with but little alteration, and can be drawn out by a siphon as needed.

From the two formulas already given we have the relations between the MnO_2, $FeSO_4$ and $KMnO_4$ as follows:

One atom of Mn in the form of brown precipitate (MnO_2) will oxidize two atoms of Fe as ferrous sulfate. Two molecules of permanganate will oxidize ten atoms of Fe as ferrous sulfate, that is to say, two molecules of permanganate will oxidize the same amount of iron as will five molecules of MnO_2 containing five atoms of manganese.

Knowing the iron value of the $KMnO_4$ and $FeSO_4$ solutions, the manganese values are easily calculated from the proportion—$Mn:2Fe = 54.93:2\times 55.84 = 0.4918$.

Determination of the MnO_2.—To the asbestos and MnO_2 in the beaker, add the solution of ferrous sulfate from a burette 5 c.c. at a time until, after stirring and warming, the MnO_2 is *completely* dissolved. It is best to take the same burette used in standardizing. Break up all lumps of asbestos and precipitate with a glass rod, as they may enclose undissolved particles of MnO_2. Now add a little water and run in the permanganate solution till a pink color is produced, not disappearing under two or three minutes. Read the burette and deduct the amount used from that to which the amount of ferrous sulfate taken would have been equivalent; the difference is equivalent to the Mn present in the precipitate. This, corrected by the factor for the permanganate solution, will give the amount of Mn in milligrams.

As an example: Suppose that 5 c.c. of ferrous sulfate solution equaled 9.6 c.c. of permanganate solution, and 10.3 c.c. permanganate equaled 0.1425 gram of ammonium ferrous sulfate. If 15 c.c. of ferrous sulfate solution were added to dissolve the MnO_2 and the permanganate required to oxidize the excess was 4.5 c.c., then the calculation is as follows:

$3\times 9.6 = 28.8 =$ the permanganate equivalent to the $FeSO_4$ used.
$4.5 =$ the "titer back."
$24.3 =$ the number of cubic centimeters of permanganate equivalent to the precipitate.

$24.3:x = 10.3:10$ (x being the true amount of correct permanganate).
$x = 23.6 = 0.0236$ gram Mn in the precipitate.

Process for Ores.—Take 5 grams. Dissolve in 50 c.c. of concentrated HCl, evaporate to dryness, avoiding a temperature above 100°; add 20 c.c. HCl, and then water. When dissolved, filter into a No. 2 beaker. Add 50 c.c. concentrated HNO_3, evaporate to a syrup, then add 100 c.c. of concentrated HNO_3 and proceed as before.

Process for Pig Iron.—Dissolve 5 grams of the metal in HNO_3 (sp. gr. 1.2) taking about 60 c.c. Then add 25 c.c. HCl, evaporate to dryness and bake. Dissolve in HCl, filter from the SiO_2, and to the filtrate add 0.2 gram ammonium fluoride or a few drops of hydrochloric acid. Then add 50 c.c. of HNO_3. Concentrate to a syrup add 100 c.c. HNO_3 and proceed as before. The hydrofluoric acid expels traces of SiO_2 from the solution and greatly accelerates the filtration from the MnO_2 (E. F. Wood).

The above process, carefully conducted, is capable of giving very accurate results, but it requires practice and should be tried on metals in which the manganese has been carefully determined by another method until the two give concordant results.

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Trans. Am. Inst. Min. Eng., **9**, 397.
Trans. Am. Inst. Min. Eng., **10**, 100.
Trans. Am. Inst. Min. Eng., **12**, 73.
Trans. Am. Inst. Min. Eng., **14**, 372.
J. Am. Chem. Soc. (1898), 504.
Am. J. Sci., **5** (4), 260
J. Anal App. Chem., **2**, 249.

Process for Materials High in Manganese.—The writer prefers to use a gravimetric method on these materials, as follows: Transfer the washed MnO_2 and asbestos mat to a beaker, dissolve the MnO_2 with 10 c.c. of HCl in 100 c.c. of water and with the addition of enough H_2O_2 to completely dissolve the MnO_2, boil until the H_2O_2 is completely destroyed, add a few drops of methyl red and then ammonia until the color turns yellow. Boil for two minutes, filter off the asbestos and small amount of iron which has precipitated and wash with 1 per cent of ammonium chloride solution. Add bromine to the filtrate, heat to boiling, filter off the MnO_2 and wash with hot water 10 times. Wash the precipitate into a weighed porcelain or silica dish, burn the filter paper and add the ash to the dish, add 10 c.c. of 1:3 H_2SO_4 and H_2O_2 until the MnO_2 all dissolves, evaporate to dryness and finally ignite to constant weight in a muffle just below red temperature, cool and weigh. The increase in weight is manganese sulfate ($MnSO_4$) containing 0.3638 manganese.

It has been shown by Blum and also by Huber that the method of weighing manganese as manganese sulfate is a method of high precision when care is taken to ignite at a temperature of 500 to 550°C.

Reference:

Huber, *Z. anal. Chem.*, **61** (1922), 103–107.

The Knorre Method for Manganese.—This method depends upon the precipitation of manganese as MnO_2 from an H_2SO_4 solution by means of $(NH_4)_2S_2O_8$ and avoids the unpleasant fumes produced by the chlorate method. As in all methods depending upon the precipitation of MnO_2, the presence of cobalt interferes as the cobalt precipitates with the manganese.

Process of Analysis.—Proceed exactly as directed in the Volhard process until the fumes of sulfuric acid are obtained. Dilute with water to 200 c.c., add H_2SO_4 if necessary to make a 5 per cent solution, add 10 grams of ammonium persulfate and boil 15 minutes. Cool, add 5 grams more and boil five minutes. Filter off the MnO_2, wash and determine the manganese as previously directed either volumetrically or gravimetrically.

Reference:

Nicolardot, *Ann. Chem. Anal. Chem. Appl.* **4** (1922), 102–110; *c.f. C. A.* **16**, 1719.

Volhard's Process for Manganese

This is a volumetric process depending upon the reactions between potassium permanganate and manganous salts by which all the manganese is precipitated as MnO_2.

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + 2KHSO_4 + H_2SO_4.$$

The method is especially applicable to high manganese ores. For low manganese ores and for iron and steels, the bismuthate-arsenite method is best.

The solution must be neutral or very nearly so. The titration must be made with the solution nearly at the boiling point and very dilute or the precipitate will not settle quickly and it will be difficult to see the end reaction. For the same reason the solution must be vigorously shaken or stirred and the permanganate added rather slowly, especially at first. Too rapid addition of the permanganate will cause the MnO_2 to precipitate on the glass, forming a firmly adherent yellow-brown stain which makes it very difficult to see the final pink color produced by the excess of permanganate when the titration is finished.

The permanganate solution used in the iron assay will serve for manganese. If 1 c.c. equals 0.01 Fe, then 1 c.c. will equal 0.002951 Mn.

In this process the iron is separated from the manganese by means of zinc oxide. ZnO precipitates the iron completely as hydroxide from a dilute solution of ferric sulfate, while manganese sulfate is not affected and remains in the solution.

Sufficient ZnO must be added to neutralize any free sulfuric acid present as well as to precipitate the iron.

The separation of the iron is really due to hydrolysis, the ZnO serving to keep the solution neutral. The reaction is:

$$Fe_2(SO_4)_3 + 3ZnO + 6HOH = 2Fe(OH)_3 + 3ZnSO_4 + 3H_2O.$$

The ZnO must not contain any alkali, as Na_2CO_3, as this would precipitate manganese.

Process for Ores.—Weigh 1.00 gram of the sample; ignite it to redness if carbonaceous matter is present; then transfer it to a casserole and digest with 15 c.c. of concentrated HCl. If any ferrous iron is present, add a few small crystals of $KClO_3$ to oxidize it to the ferric state. Finally, boil until all free chlorine is expelled. Now add 10 c.c. of dilute H_2SO_4 (1:1) and evaporate till fumes of H_2SO_4 begin to come off, then cool the casserole and add 75 c.c. of water. Warm till all of the ferric sulfate goes into solution and then transfer to a 500-c.c. graduated flask. Add a saturated solution of Na_2CO_3 to the contents of the flask until a slight precipitate appears which is dissolved in a few drops of dilute H_2SO_4. Add 10 grams of $ZnSO_4$, heat to boiling and add 1 gram of ZnO. Cool, dilute to the 500-c.c. mark, mix and decant off 200 c.c. Heat to boiling and titrate with standard $KMnO_4$, with vigorous shaking and with the liquid kept at boiling. When a permanganate color appears, cool somewhat and add 1 to 2 c.c. of glacial acetic acid when the color will disappear. Now finish the titration in the hot but not boiling solution. The permanganate color should persist after the solution has been shaken several times. The color will then persist for one to two hours.

The potassium permanganate used should be carefully standardized against an ore of known manganese content, or as follows: Dissolve 0.5 gram of Armco iron, the manganese in which has been determined by the bismuthate method, and treat the sample as directed above. After the sulfuric acid solution has been evaporated to fumes and diluted, add 0.400 gram of $MnSO_4$ obtained as directed on page 85, then proceed as directed in the Volhard method.

If the iron value of the permanganate is used to calculate the manganese value, the following calculations must be used: The permanganate when used to titrate iron in acid solution undergoes a valence change of 5, but when used to titrate manganese in a neutral or slightly acid solution, undergoes a valence change of 3, hence its oxidizing strength is only three-fifth as great as when used for titrating iron. The manganese that is being titrated undergoes a valence change of 2, hence $Mn = 2Fe$, and the final proportion used will be $Mn:2Fe::x:\frac{3}{5}$ iron value of permanganate, or the manganese value equals 0.2951 times the iron value of the permanganate.

Notes on the Process.—Where the amount of manganese in the sample is less than 0.7 or 0.8 per cent, the process is not satisfactory, unless more of the sample is taken, since the precipitate will not clot and settle properly if there are less than 5 or 6 mg. of manganese in the liquid. Therefore, in applying the process to ores or metals quite low in manganese, enough sample must be weighed out that there shall be at least this amount of manganese in the liquid titrated. The bismuthate method is much better for low manganese samples.

As more than a trace of free mineral acid interferes with the titration, the amount of HNO_3 added must not exceed that indicated or the precipitate will settle badly and the end point be indistinct. Evaporation with H_2SO_4 is necessary to destroy the carbonaceous matter as well as to expel the HNO_3, both of which may affect the titration.

Instead of taking 1 gram for the analysis, it is usually more convenient to take such an amount of the sample as will make 1 c.c. of the permanganate equivalent to 1 per cent of manganese. This amount can be calculated from the iron standard of the permanganate. Thus, if 1 c.c. of the $KMnO_4$ equals 0.01 Fe, take 0.5902 gram of the sample for the process, then the half of the solution taken for the titration will contain 0.2951 gram of the sample and each cubic centimeter of permanganate used will obviously represent 1 per cent of Mn.

For steels low in carbon, the Volhard method has been modified by omitting the evaporation with H_2SO_4 and not filtering from the precipitate of ferric hydroxide produced by the ZnO, but instead simply decanting an aliquot part of the somewhat turbid liquid and titrating directly in the presence of the nitrates. In this case the permanganate should be standardized on a steel of similar kind in which the manganese has been determined gravimetrically. High carbon steel should be evaporated to dryness with HNO_3 and baked.

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AUCHY, *J. Am. Chem. Soc.* (1896), 498.
J. Ind. Eng. Chem., **1**, 607.
ORTHEY, *Z. anal. Chem.*, **47**, 547–560.
FISCHER, *Z. anal. Chem.*, **48**, 751–760.
CAHEN and LITTLE, *Analyst*, **36**, 52–59.

THE BISMUTHATE-ARSENITE METHOD FOR MANGANESE

This method for manganese, when it is present in moderate amounts (up to 2.5 per cent), is, in the writer's opinion, the most accurate known. No elements interfere if the process is properly carried out. The delicacy of the reaction between manganese and bismuthate in HNO_3 is remarkable, as little as 0.00001 gram in 50 c.c. can be easily detected. HCl must be absent, as it is ruinous to the accuracy of the results.

The method is based on the fact that in a cold HNO_3 solution of the proper strength manganese is oxidized to permanganic acid by the bismuthate. This is very stable in cold HNO_3 (sp. gr. 1.135) but in hot solution the excess of bismuthate is decomposed and dissolved and then the permanganate is destroyed. In the cold, however, the excess of bismuthate may be filtered off and the permanganate titrated by a standard reducing agent.

The reactions may be written:

$$5Bi_2O_4 + 2Mn(NO_3)_2 + 26HNO_3 = 10Bi(NO_3)_3 + 2HMnO_4 + 12H_2O.$$
$$HMnO_4 + 2Na_3AsO_3 + 3HNO_3 = 2Na_3AsO_4 + Mn(NO_3)_3 + 2H_2O.$$

Process for Iron and Steel.—If the sample does not contain over 1 per cent Mn, use a 1-gram sample; if 1 to 2 per cent, use a 0.5-gram sample. Dissolve in 45 c.c. of water and 15 c.c. of HNO_3 (sp. gr. 1.42) in a 150-c.c. flask. When dissolved boil until nitrous fumes are gone. Set the flask off the hot plate and cool a moment, then add 0.25 gram of bismuthate and shake and continue adding the bismuthate in 0.25-gram lots until a permanganate color comes which persists after a few minutes' boiling. This indicates complete oxidation of the solution. On boiling, the permanganic acid is gradually decomposed to MnO_2. Now add a few small crystals of KNO_2 to dissolve the MnO_2 and boil the solution several minutes to expel nitrous fumes. A little Na_2CO_3 added now will aid the expulsion of the fumes. Add water to bring the volume up to its original volume and cool to tap-water temperature. When cold, add 0.5 gram of bismuthate and shake the flask well. Add 20 c.c. of water and again shake, then filter through asbestos, preferably after settling, and wash several times with distilled water.

Titrate the filtrate with standard arsenite solution. If the manganese is high, a little MnO_2 may appear at the end but this does no harm, as the titration is continued until the brown MnO_2 disappears. This only takes a drop or two after the pink disappears.

Arsenite Solution.—Add to 0.908 gram pure As_2O_3 in a beaker, hot Na_2CO_3 solution until the As_2O_3 all dissolves, then dilute to a liter. One cubic centimeter should be equal to 0.0002 gram Mn. To standardize, treat a sample of steel with known Mn content as above described.

An equally good method of standardization is as follows: Dissolve 6 grams of $KMnO_4$ in 1 liter, heat and pass H_2S through the solution until all the manganese is precipitated as MnS, filter and wash 20 times with H_2S water. Burn the paper and precipitate at a low temperature in a platinum crucible, add H_2SO_4 until the residue is well moistened, and very gradually raise the temperature of the crucible in a muffle until the H_2SO_4 is all gone and the temperature remains at 500°C. for 10 minutes, cool the crucible and weigh the $MnSO_4$. Dissolve the $MnSO_4$ in a sufficient amount of 1 per cent H_2SO_4 so that 1 c.c. contains 0.00020 gram manganese. $MnSO_4$ contains 0.3638 manganese.

Dissolve 0.5 gram of Armco iron or other pure iron in which the manganese has been determined, add 25 c.c. of the solution above prepared and determine the manganese as directed. It is not possible to make an accurate check against $KMnO_4$ directly, owing to its variable composition.

Notes on the Process.—It is necessary to add the bismuthate to the hot HNO_3 solution until all carbon, sulfur, etc. are oxidized as well as the manganese. Otherwise results will run low. This complete oxidation is indicated when the MnO_2, formed when the $HMnO_4$ is decomposed by boiling, remains after boiling a minute or so.

Chromium is partly, and vanadium completely, oxidized to the higher forms H_2CrO_4 and H_3VO_4 by the bismuthate in cold solution. These do not harm if the titration is carried out as above directed. If, however, titration is carried out by adding an excess of arsenite or other reducing agent and then oxidizing back to standard $KMnO_4$, the results will be high if chromium or vanadium are present, as the chromic acid and vanadic acid will be reduced by the arsenite. The titration should be carried out by adding the arsenite until the permanganate color just disappears.

The best material for filtering off the Bi_2O_4 is asbestos and glass wool made as follows: Shake together in a flask, with water, sufficient glass wool to fill a funnel one-fourth full and about the same amount of pure asbestos fiber. Pour into a funnel and wash out all HCl. This filtering medium does not easily stop up and yet filters perfectly. It may be used for a large number of filtrations without changing.

When pig irons are being analyzed they should be filtered when dissolved in order to remove the graphite. In the analysis of white irons it will be necessary to treat the solution several times with bismuthate in order to oxidize the large amount of combined carbon present. The solution should be nearly colorless when cold.

Process for Iron Ores.—Treat 1 gram in a beaker with 20 c.c. HCl until all iron is in solution. Add 4 c.c. H_2SO_4 and evaporate until the H_2SO_4 fumes freely, taking particular care that all the HCl is removed. Cool and dissolve in 45 c.c. of water and 15 c.c. of HNO_3, filter and proceed as in the case of steels. It may be necessary to examine the residue for manganese.

For manganese ores proceed as above except to dilute to the mark in a calibrated flask, shake well and take an aliquot part equal to 1 per cent of manganese on a 1-gram sample. However, the Volhard process is more especially adapted to high manganese ores.

REFERENCES:

BLAIR, "Analysis of Iron and Steel," 7th ed., p. 121.
DEMOREST, "The Bismuthate Method for Manganese," *J. Ind. Eng. Chem.*, **4** (Jan., 1912).
BLUM, *J. Am. Chem. Soc.*, **26**, 793.

COLOR METHOD USING AMMONIUM PERSULFATE

This method is due to Marshal and Walters. It depends upon the act that if ammonium persulfate $(NH_4)_2S_2O_8$ is added to a solution of manganese in dilute nitric or sulfuric acid, it will, on warming, promptly and completely oxidize the manganese to permanganic acid, provided a small amount of silver nitrate is present. The silver salt is essential, for, if not present, the manganese will be precipitated as MnO_2. If too much silver salt is present, silver peroxide will precipitate and make the solution muddy.

The solution should not be boiled, but merely warmed until the color develops.

It is said that the persulfate should be slightly damp, but we have used this salt dried in a desiccator with satisfactory results.

Walter's Process for Steel.—Dissolve 0.1 or 0.2 gram of the steel, according to the percentage of manganese, in 10 c.c. of HNO_3 (sp. gr. 1.2). Heat until all nitrous fumes are driven off. Now add 15 c.c. of a solution of silver nitrate containing 1.33 gram of the salt to 1 liter of water. This will cool the solution considerably. Now immediately add about 1 gram of ammonium persulfate, and warm until the color commences to develop, and then for about a half minute longer. Remove from the heat and set it in cold water while the evolution of oxygen continues. As soon as the solution is cool, compare it with a solution of standard steel treated in the same manner.

The solution of the standard steel may be prepared in quantity, as noted before, by dissolving several grams of the metal in a sufficient amount of nitric acid (sp. gr. 1.2) and diluting with the same strength acid until 10 c.c. of the solution contain 0.2 gram of steel. Ten cubic centimeters of this solution are then used with each set of determinations.

REFERENCE:

Chemical News, Feb. 15 and Nov. 15, 1911.

Persulfate-arsenite Method.—This method has the advantage of requiring no filtrations as the bismuthate method does. Proceed as above directed for the persulfate method until the ammonium persulfate has oxidized the manganese. Cool, add 10 c.c. of a 2.5 per cent NaCl solution, stir and titrate with sodium arsenite as usual. The sodium chloride is added to precipitate the silver, otherwise the excess persulfate will make results for manganese run high.

CHAPTER VII

THE DETERMINATION OF SULFUR

Sulfur occurs in iron ores as sulfides, such as pyrite (FeS_2) and sphalerite (ZnS) and also as sulfates, such as gypsum ($CaSO_4$, $2H_2O$), barite ($BaSO_4$) and celestite ($SrSO_4$). In iron and steel it occurs as sulfide only. In the gravimetric methods for determining sulfur it is first converted into sulfuric acid and then the sulfuric acid precipitated by barium chloride and weighed as barium sulfate.

Direct Oxidation Methods

Conversion of the Sulfides to Sulfates.—All sulfides are completely oxidized to sulfates when fused with a mixture of dry Na_2CO_3 and $NaNO_3$ or with Na_2O_2.

As free sulfur and certain disulfides give off sulfur vapor at a comparatively low temperature (below the fusing point of Na_2CO_3), when these are present care must be taken to prevent loss by the escape of this vapor. The mixture of ore and flux must be covered with a layer of the pure "fusion mixture" and heated carefully.

After fusion all the sulfur, whether originally present as sulfide or sulfate (even in $BaSO_4$), will be found as Na_2SO_4, the bases present remaining as oxides or carbonates. When the fused mass is boiled with water till thoroughly disintegrated and then filtered off and washed, the sulfate all passes into the filtrate.

Sulfides can be more or less completely oxidized to sulfates in the "wet way" by treating them with hot concentrated HNO_3 or aqua regia. Wet methods are not very satisfactory, as free sulfur is liable to separate and fuse to globules, its melting point being below the boiling point of HNO_3. Once in this form it is very slowly oxidized by boiling with ordinary oxidizing agents. Iron sulfide can be completely oxidized, however, by heating with a large excess of concentrated HNO_3 and adding a little powdered $KClO_3$.

When iron sulfide, or even iron containing but little sulfur, is dissolved in dilute HNO_3 (1.2 sp. gr.) a considerable proportion of the sulfur separates as such and escapes oxidation.

Solutions containing ferric sulfate, on evaporation to dryness and "baking," as is common in iron analysis, may lose SO_3 unless enough potassium or sodium is added to hold it all in combination with the alkali, as the sulfate of iron is easily decomposed by heat and SO_3 expelled.

REFERENCES:

FRESENIUS, "Quantitative Analysis."
PHILLIPS, *J. Am. Chem. Soc.* (1896), 1079.

THE PRECIPITATION OF THE SO_3 BY $BaCl_2$

This precipitation must be conducted under carefully regulated conditions, if the results are to be satisfactory.

When the amount of sulfur present is very small, the contamination of the $BaSO_4$ is not apt to be important and the chief thing is to get the sulfur completely precipitated; but when large amounts of sulfur are to be precipitated, as when pyrite is to be analyzed, the case is very different and great care must be taken to have the $BaSO_4$ pure as well as completely precipitated.

When alkalies are present, all $BaSO_4$ precipitates carry down alkali sulfates, the error being worst if alkali chlorides are present. If ammonium salts are present, ammonium sulfate is carried down, and is, of course, lost on ignition. In the presence of much alkali chloride, the precipitate contains a certain amount of free sulfuric acid. All of these errors make results run low, in some cases perhaps as much as several per cent of the total weight.

In addition to these minus errors, there are plus errors. All barium sulfate precipitates contain barium chloride. If the precipitation is made very slowly, the amount of this is very small. When the precipitation is made rapidly, it is much larger. Nitrates are occluded by barium sulfate, giving results which are high. When barium sulfate is precipitated from solutions containing much ferric iron, iron salts will adhere to the precipitate, making it reddish in color, unless considerable HCl is present. Some of the sulfuric acid appears to be in combination with the iron instead of with the barium, and is driven off on ignition, causing low results. Water alone will not wash out any of the above salts occluded with the barium sulfate.

Barium sulfate, while very insoluble in water, is not so in dilute acids, the amount dissolved increasing with the concentration of the acid, though the presence of a considerable excess of $BaCl_2$ very largely decreases the solubility of the barium sulfate in HCl. Acid solutions of $FeCl_3$, when hot, hold a little $BaSO_4$ in solution, which separates when the liquid cools.

The precipitate of $BaSO_4$ is fine, liable to run through the filter paper, if precipitated cold, and so should be precipitated hot and allowed to stand on a warm plate with frequent stirring. In this way the precipitate will grow dense and granular so that it can be easily filtered.

It will be seen from the above that the determination of sulfur when present in large amounts is attended with many difficulties and, for accurate results, correction must be made by analysis of the precipitate. For good technical results perhaps the best way is to wash the precipitate off the filter back into the beaker, add HCl equal to the water present and evaporate almost to dryness, add 100 c.c. of water and 5 c.c. of 10 per cent $BaCl_2$, let settle and filter.

REFERENCES:

HILLEBRAND, *Bull.* 422, U. S. Geol. Survey, p. 195.
ALLEN and JOHNSON, *J. Am. Chem. Soc.* (May, 1910), 588.
ARCHBUTT, *J. Soc. Chem. Ind.*, **9**, 25.
LUNGE, *J. Soc. Chem. Ind.*, **8**, 819, 967.
AUCHY, *J. Am. Chem. Soc.* (1901), 147; *Am. Chem. J.* (1902), 495.

Process for Sulfur in Iron Ores.—Mix 1 gram of the finely pulverized ore with 5 grams of dry Na_2CO_3 and 0.5 to 1 gram of $NaNO_3$, according to the amount of sulfur in the ore. Put the mixture in a platinum crucible and fuse carefully. As soon as it is well melted, chill the crucible by dipping the bottom into water. This will usually loosen the cake so that it can be removed from the crucible. See page 377.

As ordinary gas contains sulfur, fusions made over it are likely to absorb some SO_2 from the flame. Therefore, an alcohol or gasoline blast lamp should be used, or an electric muffle. If gas is used, the crucible must be kept covered during the fusion and should be protected by inserting it into a tightly fitting collar of sheet asbestos nearly to the top. This will act as a shield to prevent the products of combustion from getting into the crucible. In accurate work it is always necessary to make a blank analysis and determine the small amount of sulfur contained in the reagents or absorbed from the gas flames. Deduct this from the amount found when working on the ore.

Boil out the fusion with water until all the material is soft and no hard lumps remain. If the solution is colored by Na_2MnO_4, add a few drops of alcohol. Filter and wash well with hot water. Add HCl to the cold solution, which should have a volume of about 100 c.c. The acid should be added until the solution is just acid, then about 4 c.c. more. Now heat nearly to boiling and add 5 to 10 c.c. of a 10 per cent solution of $BaCl_2$ previously diluted with 10 to 20 c.c. of water and heated. Stir and let the precipitate of $BaSO_4$ settle several hours. When clear, filter, wash with hot water, ignite and weigh the $BaSO_4$. This weight multiplied by 0.1374 gives the amount of S.

If it is suspected that the $BaSO_4$ is contaminated with SiO_2, it should be treated with HF. It is a good thing to do in any case. Add to the ignited precipitate a drop of H_2SO_4 and 2 c.c. of HF. Evaporate off the acids and finally again ignite and weigh.

Notes on the Process.—$BaSO_4$ is easily reduced to BaS by heating with carbon. This may occur in the crucible and will make the results come low; hence, in igniting the precipitate, detach it as far as possible from the filter, burn the paper carefully on a platinum wire, avoiding a high heat. Add the ash to the precipitate in the crucible and heat gently with the cover off until all the carbon is burned, finally igniting to a bright red-heat.

Instead of drying the paper, the wet filter and precipitate may be ignited together by proceeding as follows: Put the filter paper containing the precipitate into a good-sized platinum crucible. The paper should be put in point down and open, just as it sets in the funnel. Now set the uncovered crucible over a very low flame and dry out the paper carefully. Then continue the heating to char the paper without letting it ignite. Should it catch fire, extinguish the flame by momentarily covering the crucible. When all the volatile matter is expelled, slightly increase the heat, which should not, however, exceed a dull red. The carbon will now all burn away and the precipitate become white. Finally, raise the temperature to bright redness. Cool and weigh as before. This process is called "smoking off" the filter and saves much time. It can be used safely on all small $BaSO_4$ precipitates. After weighing the precipitate, add a little water to it and test with turmeric paper. If it reacts alkaline, the results are untrustworthy, as reduction has occurred; in this case add a drop of H_2SO_4; heat till dry, ignite and weigh again, taking the second weight as the correct one.

Wet Oxidation Method for Sulfur in Ores

This method fails to determine the sulfur in any $BaSO_4$ or $PbSO_4$ contained in the ore. Therefore, it is not so generally applicable as the fusion method unless the residue is separately treated by the fusion method and any sulfur thus obtained added to that obtained by the wet method.

Process of Analyses.—Weigh 1 to 5 grams of the very finely pulverized ore. Put it in a covered casserole or beaker and add 20 c.c. of concentrated HNO_3. Heat and add 1 gram $KClO_3$ in several portions. Now digest at a moderate heat till all action ceases, then evaporate off most of the HNO_3. Add an excess of HCl and warm until the iron is all dissolved. Evaporate to dryness and proceed as with the dried residue in the determination of sulfur in iron or steel.

When sulfur is present in large amounts, as for instance, in pyrite, it is necessary that the $BaSO_4$ be precipitated from a solution free from iron. Dissolve 0.5 gram of the very finely ground sample in 20 c.c. of aqua regia in a beaker with a watch-glass cover. Heat until decomposition is complete, then evaporate to dryness. If necessary, use a little $KClO_3$ with the aqua regia to dissolve the pyrite. Moisten the dry mass with 1 c.c. HCl and 100 c.c. of water. Heat until all except the gangue is dissolved and filter. To the *cold* solution add ammonia until alkaline, heat to boiling and filter off the $Fe(OH)_3$ and wash thoroughly. Make the filtrate acid with HCl, heat to boiling and add slowly $BaCl_2$ with constant stirring. After standing some time, filter and wash, transfer the $BaSO_4$ back to the beaker, add as much HCl as there is water present, evaporate almost to dryness, add 100 c.c. water and then 20 c.c. $BaCl_2$, allow to stand a half hour, filter and wash. Ignite very carefully to prevent reduction of the $BaSO_4$.

METHOD FOR SULFUR IN IRON AND STEEL

As the sulfur is usually present in these metals in very small percentages only, its accurate determination demands great care. It is present as FeS, MnS and possibly CuS and ZrS_2.

Process of Analysis.—Take from 2 to 5 grams, according to the percentage of sulfur. Add 25 to 40 c.c. concentrated HNO_3. Cool the dish if the action is too rapid, or heat it if it is too slow. The rate of solution must not be too rapid or low results may follow.

When the metal is nearly all dissolved, heat to boiling and add 2 to 3 c.c. of concentrated HCl to complete the solution. Now add about 0.5 gram $KClO_3$ free from sulfur. Boil to dryness and bake on a hot plate 10 minutes. Add 10 to 20 c.c. concentrated HCl to dissolve the residue and again dry down thoroughly. Dissolve again in 15 to 40 c.c. of concentrated HCl. Evaporate the solution until a skin begins to form on the surface or until it become syrupy. Now add 5 to 10 c.c. of concentrated HCl, according to the amount of iron taken. When all the iron dissolves dilute the liquid with its own volume of hot water and filter into a small beaker through a paper previously washed out with a little hot dilute HCl (this facilitates filtration). Wash the dish and insoluble residue with hot water.

The filtrate and washings must not exceed 75 c.c. Now warm to about 60°C. and add 10 c.c. of a 10 per cent solution of $BaCl_2$. Let stand till the precipitate settles, leaving the liquid perfectly clear. (Four hours is sufficient if everything is right.)

Filter onto a small ashless filter, wash with water containing a few drops of HCl until the iron stain is gone, then eight times with cold water, ignite and weigh the $BaSO_4$. Test the filtrate by the addition of considerably more $BaCl_2$ solution, which must give no additional precipitate.

The residue from which the solution for the determination of sulfur is filtered must contain no basic iron salts, as these may hold sulfur. These are likely to form if the HCl solution is concentrated too far and insufficient acid is added before dilution.

REFERENCE:

J. Anal. App. Chem., **6**, 318.

Notes on the Process.—It is imperatively necessary that a blank be run on all the reagents used in the process and the weight of $BaSO_4$ obtained in this way deducted from that found in the analysis.

Certain high-carbon steels and most ferrosilicons will resist the action of concentrated HNO_3 almost entirely. When treating such metals add some potassium chlorate with the nitric acid at the start, and also at intervals add concentrated HCl, 1 c.c. at a time, until the metal is dissolved; then add more $KClO_3$ and proceed as usual.

Ferrosilicons with over 10 per cent of silicon will resist the action of all the ordinary solvents. These and other insoluble alloys cannot be treated by wet methods for the determination of sulfur.

Where the percentage of silicon does not exceed about 15 per cent, the small addition of sodium fluoride to the HNO_3, as described under "Phosphorous" on page 64, will usually bring the metal into solution and the determination can then be carried out as usual, by adding the chlorate, evaporating, baking and taking up in HCl. In other cases the metal must be fused. The fusion is best made in a platinum crucible with a mixture of equal parts of $NaNO_3$ and Na_2CO_3, using at least six parts of the mixture to one of the metal. The fusion can be then soaked out with water and the water solution treated, as in the case of an ore.

The sulfur will all go into the water solution, provided the iron is completely oxidized. It is essential that the metal be very finely powdered. The peroxide of sodium can be substituted for the nitrate or may be used alone, in which case at least 8 grams of the reagent must be used for one of metal, and the fusion made in a nickel crucible. Blanks must be run on all the reagents.

References:

F. C. Phillips, *J. Am. Chem. Soc.* (1896), 1079.
E. H. Saniter, *J. Soc. Chem. Ind.* (1896), 155.

Bamber Method for Sulfur.—This method is suitable for the analysis of cast iron or steel and for any iron alloys which are decomposed completely by treatment with nitric acid. It has proved to be a very reliable method.

Process of Analysis.—Dissolve from 3 to 5 grams of the sample in concentrated nitric acid (sp. gr. 1.42). After the iron has dissolved completely, add 2 grams of solid potassium nitrate and evaporate to dryness on the water bath in a platinum dish. Heat the residue to redness using an alcohol flame. After the ignition add 50 c.c. of a 1 per cent solution of sodium carbonate, boil for a few minutes and filter. Wash the precipitate thoroughly with hot 1 per cent sodium carbonate solution. Acidify the filtrate with HCl and evaporate to dryness. Moisten the residue with 2 c.c. of concentrated HCl and add 50 c.c. of water. Heat to boiling and filter. Dilute the filtrate to 100 c.c. and precipitate the filtrate hot with 10 c.c. of 2 per cent barium chloride solution. Ignite and weigh in the usual manner.

THE DETERMINATION OF SULFUR IN PIG IRON AND STEEL BY EVOLUTION AS H_2S

The direct oxidation methods are accurate and the only ones which can be relied upon to give with certainty the total sulfur in any material. But they are too slow to answer for control work. For such purposes the evolution methods are very generally used. They are either gravimetric or volumetric and can be made extremely rapid. For some materials they will give reliable results.

These methods all depend upon the assumption that when iron is dissolved in HCl the whole of the S is evolved as H_2S and passes off with the excess of hydrogen. This is probably true, or nearly so, for steel containing but little carbon and possibly for gray pig iron; it certainly is not true for white iron and mottled irons high in combined carbon; and probably not true for high-carbon steels and some ferro-silicons, especially those containing much sulfur.

In these latter materials part of the sulfur appears to be evolved as more or less volatile liquid or possibly gaseous compounds of carbon, hydrogen and sulfur, and not as H_2S. The proportion of the sulfur evolved as H_2S will vary in the same iron if the heat treatment has been different; if slowly cooled, it may be gray and evolve most of the sulfur as H_2S; if suddenly cooled by chilling in water (shot samples), it will be white and only a small portion of its sulfur may be evolved as H_2S. Hence, by evolution methods, the latter sample would show a much lower percentage of sulfur than the former. The sulfur that is lost is in the form of $(CH_3)_2S$, or some similar form. The higher the percentage of carbon in solid solution (Martensite) in the iron, the more sulfur is thus lost. Part of this goes over with the gases and part stays behind in the flask. If the evolved gases be passed with hydrogen through a glass tube heated to dull redness, the sulfur compounds are changed to H_2S. If the tube is filled with asbestos coated with platinum black the action is more rapid. Care must be taken to exclude air or explosion will result. The amount of sulfur evolved in combination as $(CH_3)_2S$ increases with the manganese in the sample and decreases with the phosphorus. Of that retained in the flask, part may be in this form, and if any titanium is present, some will be held in combination with the titanium. Phillips has shown that sulfur retained in the flask as difficultly volatile organic compounds may be distilled off by prolonged boiling.

By taking certain precautions the amount of sulfur lost can be reduced to a very small amount and the results by the evolution process can be made to check fairly well with the standard process even on pig irons. These precautions are as follows:

(1) The weighed sample should be annealed in a non-oxidizing atmosphere according to a certain procedure. This changes the martensite to pearlite with cementite, graphite or ferrite, according to the amount of carbon. (2) The speed of solution should be as great as possible. (3) The acid used should be concentrated acid, of sp. gr. 1.19. Under these conditions the use of a hot tube through which to pass the evolved gases is not necessary.

Ordinary low-carbon steels do not have to be annealed, but high-carbon steels, pig irons and the alloy steels, such as self-hardening steels and nickel-chromium steels must be annealed to get correct results.

For rapid work, as for furnace control, the annealing of the sample may be omitted, but it should be understood that this always gives low results, sometimes as much as 20 per cent low when the sample is a pig iron.

On the other hand, in the case of steels, the results for sulfur by the evolution process may give too high results. Besides H_2S, other gases are given off which may affect the results. These are hydrocarbons and PH_3 and AsH_3, which are absorbed to a certain extent and affect iodine used for titrating, but do not affect gravimetric results. According to Elliot, these are not absorbed in $CdCl_2$ solution containing acetic acid and ammonium acetate as they are in alkaline solutions or in solutions of lead, zinc or copper.

The H_2S evolved is very easily decomposed by comparatively feeble oxidizing agents, water being formed and free sulfur deposited. *Prolonged* contact with air and sunlight, the presence of $FeCl_3$, traces of chlorine, all act on it in this way, and must be avoided in the process. There is no necessity, however, of working in an atmosphere of hydrogen or of carbon dioxide if the process is *rapidly conducted.* On the other hand, slow evolution, or the use of HCl containing traces of chlorine or $FeCl_3$ will cause decomposition of the H_2S and retention of sulfur in the residue.

Rusting of the drillings previous to the addition of HCl leads to the formation of $FeCl_3$ and may cause a separation of sulfur from the gas in the flask. Dilute HCl (1:1) is usually used in these methods but, according to the writer's experience, this sometimes fails to cause complete evolution of the sulfur as H_2S where the concentrated acid succeeds. (See PHILLIPS, *J. Am. Chem. Soc.* (1895), 891.)

While the H_2S is easily absorbed, the organic sulfur compounds are only slowly and incompletely taken up. Long boiling is frequently necessary to drive them completely out of the flask in which the iron is dissolved. It is evident from what has been said that the evolution processes are reliable only when they are checked by using the gravimetric process on the same kind of sample.

The H_2S evolved may be determined in many ways. It may be absorbed in an alkaline solution of lead acetate, then oxidized to SO_3 and precipitated by $BaCl_2$, or it may be absorbed in a solution of HCl and bromine and the H_2SO_4 formed precipitated by $BaCl_2$, or in an alkaline solution of $KMnO_4$ and precipitated as before. Some chemists absorb the H_2S in a $CuSO_4$ solution, filter off the copper sulfide, ignite and weigh as CuO. The most widely used method is, however, a volumetric one in which the H_2S is titrated with a standard iodine solution. It is very rapid and is quite as accurate as the other evolution methods.

The Iodine Method for Sulfur

The H_2S may be absorbed in NaOH or KOH or an ammoniacal solution of zinc or cadmium. The cadmium solution is preferred because it fixes the sulfur in a visible form and is not easily altered on standing. KOH and NaOH are liable to contain oxidizing impurities, such as nitrites or ferric hydroxide, which would oxidize H_2S.

The reactions involved in the process are as follows:

$$\mathrm{FeS(or\ MnS) + 2HCl = FeCl_2(or\ MnCl_2) + H_2S.}$$
$$\mathrm{H_2S + CdCl_2 = CdS + 2HCl.}$$

The HCl liberated is neutralized by the NH_4OH present. When the H_2S has all come over, the solution is diluted and strong HCl is added in excess; then the reverse reaction takes place,

$$\mathrm{CdS + 2HCl = H_2S + CdCl_2.}$$

A considerable excess of HCl is necessary to dissolve completely all of the CdS. The volume of the solution should be very large to prevent the escape of the liberated H_2S. Also it should *not* be *hot*.

The H_2S is then titrated with iodine.

$$\mathrm{H_2S + 2I = 2HI + S.}$$

The liberated sulfur causes the liquid to become curiously opalescent and show various colors, but this does not at all obscure the end reaction, which is very sharp. Before titration a little starch solution is added to the liquid to be titrated. One drop of iodine in excess of the amount required to titrate the H_2S causes an intense blue color of "starch iodide" to be formed.

Preparation of the Starch Solution.—Stir 5 grams of wheat starch into 200 c.c. of cold water. Heat the liquid to boiling with constant stirring until the starch is thoroughly dissolved. Now dilute the liquid with cold water to about a liter, and add 10 grams of crystallized $ZnCl_2$. Let the solution settle for some time, and pour off for use the nearly clear supernatant liquid. This solution is very sensitive and keeps indefinitely.

A solution of 1 gram of starch in 200 c.c. of boiling water alone may be used, but it must be made fresh every day.

For a more sensitive preparation of starch, see page 188.

Preparation of the Iodine Solution.—Weigh on a watch-glass 1.13 grams of KIO_3 and dissolve in 300 c.c. of water containing 12 grams of KI and 1 gram of KOH. When dissolved, dilute exactly to 1,000 c.c. The solution keeps well. When added to an acid solution for titration the reaction is

$$KIO_3 + 5KI + 6HCl = 6I + 6KCl + 3H_2O.$$

One cubic centimeter will titrate approximately 0.0005 gram of S.

Cadmium Solution.—Dissolve 4 grams of cadmium chloride in 100 c.c. of water, and when dissolved add an equal volume of strong ammonia.

Standardizing the Iodine Solution.—Prepare the following solutions:

A. Dissolve 8 grams of crystallized sodium thiosulfate in water and dilute to 1 liter.

B. Dissolve 0.1531 gram of fused potassium dichromate in water and dilute to 100 c.c. If more convenient, this solution may be made by diluting 10 c.c. of the dichromate solution used in the iron assay (of which 1 c.c. equals 0.01 Fe) to 57.42 c.c.; 10 c.c. of this solution will liberate iodine from KI equivalent to 0.005 gram of sulfur.

Measure with a pipette 10 c.c. of the thiosulfate solution A into a beaker. Add 100 c.c. of water and 1 c.c. of starch solution, now run in the iodine solution from a burette until nearly the amount required to oxidize the thiosulfate has been added, add 5 c.c. of HCl and continue the addition of iodine solution until the last drop gives a decided blue color not disappearing on stirring. Note exactly the amount used. Repeat the determination two or three times (the results should agree almost exactly) and take the average as the amount of iodine solution equivalent to 10 c.c. of the thiosulfate.

Measure 10 c.c. of the dichromate solution B into a beaker. Add 50 c.c. of cold water and then about 0.5 gram of pure KI. When the KI is dissolved, add 5 c.c. of concentrated HCl.

The KI must be free from iodate. It may be tested by dissolving a portion in water, adding some starch solution and a little HCl. The liquid should not show more than a trace of blue color and should become absolutely colorless on the addition of a small drop of the thiosulfate solution. The acid must be free from chlorine or ferric chloride. When diluted it should give no blue color on the addition of KI and starch.

Let the mixture stand six or seven minutes without warming (which would volatilize iodine). Dilute to 100 c.c. and add 10 c.c. of solution A and 1 c.c. of starch solution. Should this color the liquid blue, add 10 c.c. more of the thiosulfate solution which will make it colorless. The first 10 c.c. is usually sufficient. Now *immediately* titrate the excess of thiosulfate with the iodine solution, adding it till the blue color is developed. Note exactly the volume of the solution used; call it R.

It is important that there be no delay between the addition of the solution A and the iodine titration on account of the presence of free HCl in the liquid. Thiosulfate is slowly decomposed by HCl with the separation of sulfur and the formation of H_2SO_3, which absorbs twice as much iodine.

By keeping the excess of thiosulfate small and titrating it within one minute, correct results can be obtained.

Now the difference between R and the number of cubic centimeters of the iodine solution which are equivalent to the number of cubic centimeters of the thiosulfate solution A added to the dichromate and iodide, as above, is the volume of the iodine solution which is equivalent to 0.005 gram of sulfur, and 0.005 divided by this difference is the value in sulfur of 1 c.c. of the iodine solution. This is the factor by which to multiply the number of cubic centimeters taken in the analysis in order to obtain the amount of sulfur present.

Example.—Suppose 10 c.c. of solution A equals 10.6 c.c. iodine solution. Second, that 20 c.c. of A were added to the 10 c.c. of B and the KI, and that the mixture required 9.8 c.c. of iodine solution on the titration back; that is, R equals 9.8. As the 20 c.c. of A alone would equal 21.2 c.c. of iodine, we have $21.2 - 9.8 = 11.4$, which is the number of cubic centimeters of iodine solution equivalent to 0.005 of sulfur, because this is the sulfur equivalent to the iodine that is liberated from the KI by the dichromate. Further, 0.005 divided by 11.4 equals 0.000439, which is the amount of sulfur to which 1 c.c. of the iodine solution is equivalent.

The reactions upon which this process of standardizing depend are:

1. $2Na_2S_2O_3\ 5H_2O + 2I = 2NaI + Na_2S_4O_6 + 5H_2O$. (The crystallized thiosulfate contains 5 molecules of water.)

2. $K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 6I$.

The thiosulfate solution is not constant, hence cannot be used as an absolute check on the iodine solution, but only as a means of comparing it with an absolutely known amount of iodine. This definite amount of iodine is obtained from the action of dichromate on an excess of KI in the presence of HCl. The reaction between KI and $K_2Cr_2O_7$ is not instantaneous, but rapidly becomes complete.

The relation between the $K_2Cr_2O_7$ and the I is 294.2:761.5, hence 0.01531 $K_2Cr_2O_7$ will liberate 0.0396 gram of iodine, the amount which should be present in 10 c.c. of the iodine solution if its strength were exactly right.

The operation itself consists, therefore, in finding how much of the iodine solution to be standardized is required to titrate the amount of the thiosulfate solution which is equivalent to exactly 0.0396 gram of iodine, as liberated by the dichromate. Thus we find *first* how much of the iodine solution is equal to a certain amount of the thiosulfate solution; *second,* how much of the same iodine solution is equal to what is left after the same amount of thiosulfate has been acted upon by 0.0396 gram of iodine, and the difference is obviously the amount of iodine solution which contains 0.0396 gram of iodine, that is to say, will be equivalent to 0.005 of S; but this should be 10 c.c., hence the difference between 10 and the amount taken is the amount the solution is off the standard.

The only precautions to be noted are the necessity of giving *time* for the $K_2Cr_2O_7$ to react on the KI and the necessity of avoiding *heat,* as iodine is readily volatilized from this solution.

The HCl used must be free from all impurities which liberate iodine from KI (Cl_2, $FeCl_3$, $CuCl_2$, etc.).

The iodine solution must also be standardized against a sample of iron or steel similar to that to be analyzed, in which the sulfur has been accurately and repeatedly determined by the direct oxidation or nitric acid method.

Treat 5 grams of the metal by the regular process and determine the volume of the iodine solution required to titrate the H_2S evolved. Then from the known sulfur percentage in the metal calculate the sulfur value of 1 c.c.

Make a factor of correction to apply to the iodine solution. This method of standardizing has the advantage of causing all errors of solution, evolution and oxidation to affect the standard and sample alike, and makes the evolution method give results comparable with the gravimetric method. It should always be used where a material of generally uniform character has to be tested as manufactured. As the heat treatment and the nature of the metal cause differences in the percentage of sulfur evolved as H_2S, an iodine solution standardized on metal should never be used for a metal made by a different process, as, for example, one standardized on pig iron for steel. (See Wilson, J., *Ann. App. Chem.*, **5**, 439). When the sample is annealed, the method of standardization does not make so much difference.

Apparatus.—This is shown in Fig. 6 and consists of a flask *F* of 500 c.c. capacity and fitted with a rubber stopper, a glass funnel tube *G* provided with a stop-cock, and a delivery tube *H*, in which are blown two or three good-sized bulbs. These bulbs serve to arrest the liquid condensing in the tube and allow it to return to the flask instead of working over into the absorption tubes. A water-cooled condenser is better. The delivery tube should carry the gas down to the bottom of a large test-tube *I*, 8 in. deep and 1¼ in. wide and fitted with a rubber stopper through which a second tube carries the gas into a second smaller test-tube *J*, which serves to catch any absorbable sulfur compounds escaping the first test-tube. This guard tube will rarely show any sulfur. Gas which is used to drive over the last trace of H_2S is introduced through *G*, in the top of which is fitted a one-hole rubber stopper with a glass tube connected to a source of gas.

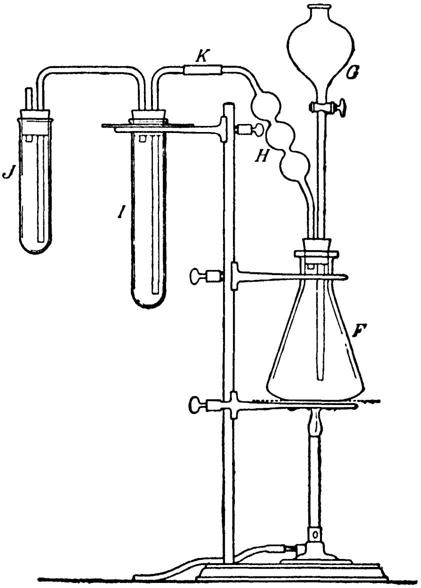

Fig. 6.

In place of the receiving cylinder or test-tube, some use a large flask, diluting the absorbing liquid correspondingly. The titration can then be made in the same flask without transferring the liquid. When the bubbles do not pass through a considerable depth of liquid, as when a flask is used as a receiving vessel, it is best to have the delivery tube in the vessel end in the form of a funnel to keep the gas longer in contact with the liquid.

Amount of Metal Taken.—This may be 5 grams for ordinary irons or 10 grams if the sulfur is very low. If the iodine solution is a little "off the standard"—that is, if 10 c.c. are equal to a little more or less than 0.005 gram of sulfur—it is more convenient, instead of correcting each reading by multiplying it by its true sulfur value, to change the amount of the sample taken so that 1 c.c. of the iodine solution shall represent 0.01 per cent of sulfur.

For example: Suppose that the iodine solution is too weak and that 1 c.c. is only equal to 0.0004854 gram of sulfur instead of 0.0005 gram. In this case weigh out 4.854 grams of the metal for the determination. Then, obviously, each cubic centimeter of the iodine solution used in the titration will stand for 0.01 per cent of sulfur, and the calculations which would be necessary if 5 grams had been taken will be avoided.

The foregoing method of applying the correction factor of a volumetric solution to the amount weighed out may be applied to any similar process; as, for example, in the determination of iron, phosphorus or manganese; and, where many analyses are to be made, will save much time as well as diminish the chances of error involved in the calculations.

Process for the Analysis.—Transfer the weighed metal to the flask and add about 2 grams of pure precipitated $CaCO_3$. Pour 5 c.c. of the cadmium solution into the absorbing tube and add to it 10 to 15 c.c. of strong NH_4OH. Now fill the tube with water to a depth of 6 in. Put 50 c.c. of HCl, sp. gr. 1.19, into the bulb of the funnel tube. Run in the acid slowly until the $CaCO_3$ is all dissolved, then run the acid in rapidly but avoid so rapid an evolution of gas as to throw the liquid out of the tube or make bubbles large enough to fill the tube. When the evolution of gas slows up, heat the flask hot enough to make the evolution of gas rapid, but do not boil until the iron is all dissolved, as this would cause too much acid to distill over. When the iron is dissolved, boil the solution for several minutes. For the best results pass a stream of hydrogen or carbon dioxide or natural gas (purified by passing through NaOH solution) through the apparatus to drive out all traces of H_2S. The solution in the tube must be kept alkaline by adding more ammonia if necessary. The CdS should separate as a yellow precipitate. If it is pale in color, the sulfur is not being evolved properly as H_2S.

When using concentrated HCl, a considerable amount of acid distills over unless a water-cooled condenser is used, but, by using sufficient NH_4OH, it will do no harm. After the liquid has been boiled several minutes and no more gas is coming over, open the stop-cock in the funnel tube, remove the lamp, and detach the delivery tube. Empty the absorbing tube into a large flask, wash it and the delivery tube well with water and pour the washings into the flask. Now add 300 or 400 c.c. of cold water, and then HCl enough to make the solution acid and 10 or 15 c.c. more, which should dissolve the precipitated CdS. Now add 1 c.c. of the starch solution and titrate immediately with the iodine solution, adding it until the last drop changes the opalescent liquid to a deep blue not disappearing on standing two or three minutes.

The number of cubic centimeters used, after correction for standard, will give the amount of sulfur in hundredths of a per cent. Always make a blank test on the reagents; they will usually consume a little iodine which must be deducted from that used in the analysis.

Notes on the Process.—Use pure gum rubber tubing in the connections. White or red rubber may contain metallic sulfides evolving H_2S when acted upon by the HCl vapor, thus causing errors.

It is essential that the process be carried through promptly. There should be no delay in titrating. If the solution containing the CdS be allowed to stand it may lose H_2S or the sulfides may oxidize. This is especially important after the addition of HCl, as the free H_2S will oxidize very rapidly on standing. Zinc salts (acetate or sulfate) may be used in the place of cadmium with satisfactory results.

The Use of NaOH Instead of $CdCl_2$.—The process is conducted as before, except that the absorption tube is filled with 80 c.c. of a 15 per cent solution of NaOH. After the evolution of the gas, wash out the tube into a large beaker, dilute as before with cold water, acidify, add starch solution and titrate. Most caustic soda contains a little iron as ferric hydroxide, which dissolves in the concentrated solution but separates on dilution; hence, the 15 per cent soda solution should be prepared some time before use, and the clear liquid decanted from the precipitate which usually settles. Test the solution also for nitrites and hypochlorites by acidifying a portion with HCl, and then adding KI and starch paste. It must show no blue color. In acidifying the soda solution before titration, add a drop of phenolphthalein solution, and then add the HCl till the red color is discharged. The HCl must be pure. It will occasionally contain traces of SO_2 which would, of course, vitiate the results.

The cadmium method is sometimes modified by filtering off the CdS and putting the filter and precipitate into a large volume of water adding HCl and titrating. This avoids the presence of a large amount of ammonium salts and of any hydrocarbons absorbed in the liquid. It has been claimed that these act slightly on the iodine. The advantage of this modification is very slight if any, as the evolution process usually gives low results any way.

The method as above given is very rapid, but gives accurate results only on those samples which give up all their sulfur as H_2S. The following method, first proposed by Walters and Miller, and modified by many others, is the method elaborated by ELLIOT (*J. Iron Steel Inst.* (1911), 412) and is good for all kinds of samples.

Annealing-evolution Process.—Five grams of the sample are mixed with 0.25 gram of pure finely powdered anhydrous potassium ferrocyanide, and wrapped in one 11-cm. filter paper, if the sample is a graphitic iron, or two papers, if it is a steel or white iron, placed in a small porcelain crucible, covered with a lid and annealed at 750 to 850°C. (just above the recalescence temperature) for 20 minutes in a muffle. The crucible is removed and allowed to cool slowly. The drillings should still be covered with charred paper. The drillings are now transferred to the evolution flask and the process continued as described for the evolution process above. Instead of using an alkaline cadmium chloride solution, Elliot uses the following: 20 grams of $CdCl_2$ are dissolved in water and NH_4OH added until the $Cd(OH)_2$ dissolves. Then acetic acid is added until the liquid is acid, then 20 c.c. more. The solution is diluted to 1,000 c.c. For each determination 50 c.c. are used. According to Elliot, this solution does not dissolve hydrocarbons, phosphides, etc., as alkaline solutions do.

This process gives good results even on alloy steels and titaniferous pig iron.

REFERENCES ON THE EVOLUTION PROCESS:

ELLIOT, *J. Iron Steel Inst.* (1911), 412.
ORTHEY, *Z. angew Chem.*, 1359–64, 1393–9.
KINDER, *Stahl. u. Eisen*, **28**, 249–254.
Trans. Am. Inst. Min. Eng., **10**, 187 (cadmium); **12**, 507 (bromine)

Determination of Sulfur in Ferro-alloys.—Fuse 1-gram sample of ferromolybdenum, ferrotitanium or ferrovanadium in a platinum crucible with 10 grams of sodium carbonate and 1 gram of sodium nitrate thoroughly mixed. After fusion is complete, thoroughly disintegrate the cake with 150 c.c. of hot water. Filter and wash well with a hot 2 per cent sodium carbonate solution. Acidify the filtrate with HCl, using 5 c.c. excess. Heat to boiling and add barium chloride to precipitate the sulfur as usual. A blank determination, of course, must be made.

Sulfur in ferromanganese is determined as directed for the gravimetric method for iron and steel. This is also true of spiegel and silico-spiegel and ferrosilicon.

For ferrochromium fuse as directed for phosphorus. Dissolve the fusion in water, acidify with HCl, reduce chromium with hydrogen peroxide until the yellow color is gone (to obtain a purer precipitate). Precipitate the sulfur with barium chloride as usual.

Sulfur in Ferrotungsten.—Dissolve a 2-gram sample in a platinum dish with 15 c.c. of nitric acid and with the addition of HF, a few drops at a time, until the alloy dissolves, evaporate nearly to dryness, add 10 c.c. of HF and again evaporate nearly to dryness; then evaporate twice with HCl, dilute to 250 c.c. in a beaker, add 10 c.c. HNO_3, evaporate to 15 c.c., add 50 c.c. of water and 5 c.c. of sulfur-free cinchonine solution, heat nearly to boiling and filter washing with hot dilute cinchonine solution. Evaporate the filtrate to dryness, add 30 c.c. HCl and evaporate until syrupy. Add 4 c.c. of water, filter and wash with hot water, precipitate the sulfur in the filtrate as usual.

REFERENCE:

U. S. Steel Corporation, "Methods for Analysis of Ferro-alloys."

CHAPTER VIII

THE DETERMINATION OF CARBON IN PIG IRON AND STEEL

The carbon in gray pig iron occurs mostly as mechanically admixed graphite, with a small proportion as a carbide Fe_3C, called "cementite," present in the eutectoid called "pearlite." In white iron and chilled iron, as well as in steel, the carbon exists chiefly either as a carbide or in solid solution, forming the phase known as "austenite," or its transition form called "martensite." Malleable iron (made by prolonged annealing of white iron) contains carbon in a more finely divided form than graphite, but not in combination with iron. Unquenched steel contains practically all its carbon as "pearlite."

When an iron containing carbon in these different conditions is dissolved in hot HCl or HNO_3 (sp. gr. 1.2) the graphite and amorphous carbon are entirely left as a black residue which can be filtered off, while the combined carbon stays in solution entirely if HNO_3 is used, but passes off partly as hydrocarbon if HCl is used. A trace of CO adsorbed in the steel also passes off.

Methods are here given for the determination of "total carbon," "combined carbon" and "graphite carbon."

Determination of Total Carbon

The total carbon is usually determined by one of the following methods:

1. Direct oxidation of the iron and carbon in some form of a furnace in a current of oxygen. The drillings may or may not be mixed with an oxidizing agent such as Pb_3O_4 or CuO in order to insure complete combustion, or with some flux to permit the oxygen to oxidize the iron completely.

The CO_2 liberated may be caught in an alkaline solution and weighed, or it may be absorbed in an alkaline solution of known strength and the excess of alkali titrated by standard acid, or, finally, the CO_2 may be measured by gas volumetric methods. The last method is not widely used.

2. The iron is dissolved in a solvent, generally K_2CuCl_4, which leaves all the carbon, whether free or combined, undissolved. The carbon is filtered off on asbestos and burned to CO_2 and determined as above.

The burning or oxidation of the carbon may be done either in a furnace (including such devices as the Shimer crucible) or it may be done by a wet process, as by combustion in sulfuric and chromic acids.

3. Solution and simultaneous oxidation of the sample in sulfuric, chromic and phosphoric acids, the CO_2 being either measured or weighed.

4. When the carbon is present entirely as combined carbon, as in steel, it may be determined colorimetrically.

DIRECT COMBUSTION METHOD FOR CARBON

This is the method most widely in use. When used with proper precaution it is very accurate and very rapid. A complete determination can be made in 10 minutes or less.

The complete combustion of steel drillings is dependent upon the temperature of the furnace. With sufficiently high temperature any ordinary steel can be completely burnt in a stream of oxygen without using red lead or CuO. The temperature ordinarily attainable, however, is not sufficient to burn completely such alloys as ferrochrome, etc., and such samples must be mixed with red lead. Pig iron also requires some copper oxide. The drillings should not be too coarse or combustion is apt to be incomplete. They should go through a 20-mesh sieve, although the writer has had no difficulty with coarser samples when the temperature of the furnace was 1,050°C. Some chemists place the drillings in as compact a mass as possible in order that the heat of the burning iron may keep it at a high temperature. This will cause the mass to fuse unless the flow of oxygen is carefully regulated, and enclose particles of unburned iron and also destroy the boat. The writer prefers to scatter the drillings along the boat and then maintain a high enough temperature in the furnace to insure complete combustion. Some chemists mix the drillings with ignited alumina or Mn_3O_4 in order to keep the drillings separated.

Such alloys as ferrochrome, ferromolybdenum, ferrotungsten and the "high-speed steels" cannot be accurately analyzed for carbon by the methods involving solution in K_2CuCl_4, as hydrocarbons are evolved upon solution. So they must be analyzed by some form of direct combustion. (See JOHNSON, "Chemical Analysis of Special Steels, Steel-Making Alloys and Graphites," p. 132 *et seq.*)

Apparatus Used.—Either gas-heated furnaces or electrically heated furnaces may be used. The writer prefers the electric furnace because of the ease with which the temperature may be controlled and because it does not heat up the laboratory noticeably. The bars on the rheostat are numbered and this apparatus is calibrated so that each number corresponds to a certain temperature in the furnace. This avoids the continual use of a pyrometer.

The carbon train shown in Fig. 7 is as given in "Method of the Chemists of the U. S. Steel Corporation for the Sampling and Analysis of Pig Iron and Steel."

A is a high-pressure oxygen tank. The oxygen made by the processes which separate oxygen from the nitrogen of the air by refrigeration is quite free from carbon usually.

B are pressure reducing and regulating valves. These are quite necessary if the oxygen is to be used directly from the high-pressure tank.

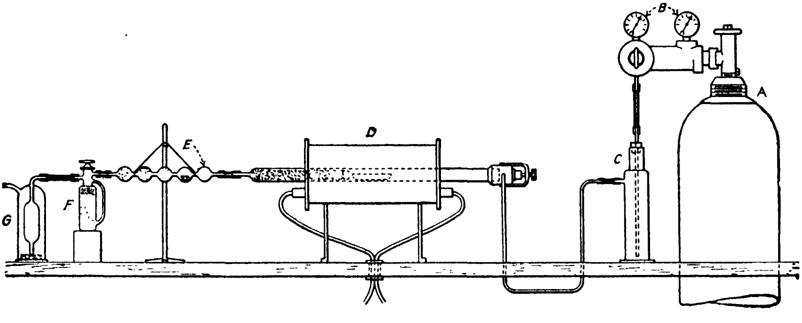

FIG. 7.

C is a purifying bottle. It is filled with soda lime to remove any CO_2 which the oxygen may, but does not usually, contain.

D is the combustion tube and furnace. The furnace is an electrically heated one, such as is made by the Hoskins Company. The current used for heating is controlled by a rheostat and, if necessary, after stepping the voltage down with a transformer.

The combustion tube in the furnace, and in which the combustion of the sample takes place, is made of fused silica or dense clay (Johnson's combustion tubes) and preferably has one end drawn out to an outside diameter of 5/16 in. so that a rubber tube will fit over it. The right-hand end is closed with a special brass plug, as shown in the figure, or by a two-hole rubber stopper. Through one of the holes the inlet tube for the passage of the oxygen is placed and through the other a glass tube with a bulb on the inside of the furnace is inserted. Through this bulb a small stream of water is circulated during the determination to keep the rubber cool.

The combustion tube is 24 in. long and 7/8 in. in internal diameter. The half of the tube at the exit end is packed with asbestos impregnated with iron oxide prepared as follows: Saturate shredded asbestos with a 10 per cent solution of ferrous sulfate, dry and ignite at 1,000°C. until all SO_3 is expelled. The iron oxide oxidizes any carbon monoxide which might be made during the combustion of the sample to carbon dioxide, causes the oxidation of sulfur dioxide to sulfuric anhydride and the asbestos also protects the rubber connection at the end of the tube from the heat of the furnace. The SO_3 combines with the iron at the cooler part of the furnace and is removed from the gas stream. Occasionally, the iron-impregnated asbestos should be removed after a hundred or more combustions and ignited to remove the accumulated sulfate. Behind the asbestos packing is placed a plug of nichrome gauze to hold it in place. It is well, though not essential, to place a sleeve of sheet nickel in the central part of the tube where the combustion boat is placed to protect the silica walls from the fluxing action of the iron oxide which is spattered during combustion. The nickel must be ignited at 1,000°C. for several hours to remove carbon.

E is a drying tube containing phosphorus pentoxide to remove all water from the gas stream going to the weighing apparatus. The form shown is better than a vertical tower because the P_2O_5 reacts with moisture from the gas, producing liquid H_3PO_4, which runs to the bottom and tends to stop up a vertical tower. When the carbon is to be determined by titration instead of by gravimetric methods, the drying tube may be omitted.

F is the weighing and absorption bottle. It is prepared as follows: Place a layer of glass wool 1/2 in. thick on the bottom. Fill the bottle to about 1 in. from the neck with "soda asbestos," cover the "soda asbestos" with a 1/4-in. layer of asbestos and then fill the rest of the bottle to the neck with phosphorus pentoxide and cover this with a layer of asbestos packed down lightly. The soda asbestos may be obtained from the chemical supply houses.

G is an "indicator bottle" of $Ba(OH)_2$. This shows the rate the gas is passing through the train and also immediately shows when the absorbing bottle is failing to function properly, as any CO_2 escaping the absorbing bottle will cause a precipitate of $BaCO_3$ to form. It is well to put a $CaCl_2$ tube between the absorbing bottle and the indicator bottle to prevent water vapor from working back into the P_2O_5.

Attach an aspirator bottle to the end exit of the train with the bottle filled with water.

Process of Analysis.—After the furnace is heated up to 1,000°C. the aspirator is opened while the tube at the inlet end is closed. If the apparatus is tight, no bubbles will pass through the indicator bottle after a few minutes. If it is not tight, it, of course, must be made so. Disconnect the aspirator and pass oxygen through at the rate of four or five bubbles per second for several minutes, detach the weighing bottle and weigh, using a similar apparatus as a counterpoise. Again attach the weighing bottle, aspirate through 1,000 c.c. of oxygen, detach and again weigh. There should not be either gain or loss in weight. If there is none, everything is ready for the determination.

Weigh 2 grams of the proper sized sample. Pour into a boat, preferably one of alundum or silica, pure alundum sand enough to cover the bottom of the boat and heap up against the sides when a trough is made in the sand with a spatula. The sand should be fine enough to pass through a 30-mesh sieve. Scatter the sample drillings in this trough so they do not heap up above, and do not touch the boat. Open the furnace tube at the inlet end, quickly push the boat to the middle of the furnace and close the tube and connect to the oxygen supply. As soon as the oxygen gets to the sample, combustion commences rapidly, and the oxygen will flow in with a rush, causing such rapid combustion of the iron that it will fuse unless the flow of oxygen is regulated. It should be so regulated that 2 grams of iron burn completely in three to four minutes. The end of the combustion is shown when the oxygen begins to flow rapidly through the $Ba(OH)_2$ bottle. If the combustion has been complete, about 650 c.c. of oxygen will have been used. During the combustion period, very little oxygen will be flowing through the $Ba(OH)_2$ bottle, but a small amount should do so. After the combustion period, continue to pass oxygen or air through for five minutes. Detach the weighing bottle and weigh. The weighing must be done promptly when the ends are not capped. If the apparatus is weighed filled with oxygen it should be capped; if filled with air, the caps are not necessary. The increase in weight multiplied by three-elevenths gives the amount of carbon present.

In order to save oxygen, air may be aspirated through before and after the combustion, but this takes more time. The soda-asbestos bottle may be filled with air by detaching from the furnace and drawing through air, dried by first passing over calcium chloride. If the bottle is weighed filled with oxygen before the combustion, it must also be weighed with the same gas after the combustion. It should be counterpoised on the balance with another similar weighing bottle.

The weighing apparatus is again attached, the boat and its contents removed from the furnace and all is ready for the next determination. The weighing bottle can be used 200 to 400 times before it needs to be refilled.

In the case of pig iron and many alloys, the process is just the same as above given, except that an equal weight of CuO is mixed with the drillings.

Notes on the Process.—The ends of the combustion tube may be kept cool by being wrapped with asbestos cloth, the ends of which dip in a beaker of water. It is also well to have a plug of asbestos in front of the stoppers to protect them from heat radiation from the walls of the tube.

Steel drillings and red lead should not be spilled in the tube, as they combine with the silica and destroy the tube. It is well to have a little silica sand scattered about the bottom of the tube to combine with spilled material.

The sand and red lead used should be thoroughly ignited before use in order to remove any carbon. The same is true of the boat.

The boats used may be molded of clay or may be made of silica, porcelain, alundum or platinum. The writer prefers the alundum, clay or silica boats. Each one should last for many determinations when properly protected with sand. Boats made of molded asbestos are sometimes used.

While, as a rule, it is not necessary to use Fe_2O_3 in the furnace, it is safest to do so in order to burn any CO which may have been formed. CuO may also be used. It may be used without injuring the silica tube as follows: A roll of CuO gauze is wrapped with asbestos paper and then placed in the tube on pieces of broken alundum boats. The CuO should be well within the furnace. A plug of palladiumized asbestos completes the precautions for complete combustion of any CO possibly present, and also protects the stopper on the exit side of the furnace from heat radiation. The palladiumized asbestos is made as directed on page 337.

Asbestos impregnated with iron oxide is more convenient and just as effective as the CuO method.

The temperature of the furnace should be not less than 950° and preferably as high as 1,050°C. At lower temperatures, combustion of the sample is not complete.

Instead of a silica tube, a porcelain one may be used. Porcelain breaks more easily than the silica tube when heated or cooled. Platinum tubes are used in some works and are very desirable, but their first cost is very high. Johnson's clay tubes are very satisfactory.

It must be remembered that the CO and CO_2 dissolved in steel will be included in the carbon obtained by this method. This may make the results as much as 0.05 per cent too high.

When the apparatus shown in Fig. 7 is used, it is possible to carry out the combustion extremely rapidly, passing through as much as 400 c.c. of oxygen per minute. When this extremely rapid method is used the iron fuses. When the oxygen rate is limited to four or five bubbles per second the drillings do not fuse and a longer time is required, but combustion is as complete.

It has been shown by the U. S. Bureau of Standards that for perfect results the burnt drillings left after combustion should be removed, ground in an agate mortar and a second combustion carried out. This is especially true of the high alloy steels.

BARIUM CARBONATE METHOD FOR CARBON

On damp days it is difficult to weigh a large absorption apparatus accurately on account of the varying amounts of moisture on the surface of the glass at different weighings. Consequently, many chemists prefer to absorb the carbon dioxide in barium hydroxide solution and weigh or titrate the $BaCO_3$. This is carried out as follows:

Process of Analysis.—In place of the weighing apparatus, attach a Meyer tube (*M*, Fig. 8) in which has been put 100 c.c. of a saturated $Ba(OH)_2$ solution. Carry on the combustion as directed above, and when the CO_2 has all been absorbed filter off the $BaCO_3$ according to the following directions. Connect the absorption bulb as shown in Fig. 8. *S* is a two-way stop-cock connected with suction. The bubble tube (Meyer tube) is fitted with two rubber stoppers through which short pieces of glass tubing pass. The filter *C* contains an ashless filter paper. Insert the stopper in the funnel and connect it with the Meyer tube, as shown in the drawing, and apply very gentle suction. When necessary open P_3 to admit air back of the liquid after the contents of the tube have all been transferred to the filter bottle, half fill the large bulb nearest *B* with water by opening the pinch-cock P_1; operate the stop-cock *S* during this and subsequent operations so as to maintain gentle suction. Manipulate the tube *M* so as to bring the wash water into contact with all parts of the interior and then suck out the water through *C*; during this and the subsequent washings leave the pinch-cock P_2 open. After eight washings, allowing the wash water to drain off thoroughly each time, detach *M* and complete the washing by filling *C* to the top with water free from carbonic acid, sucking dry and repeating the operation once more.

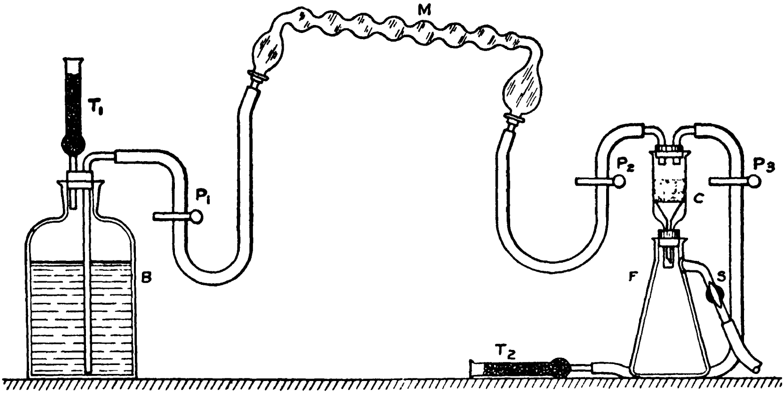

FIG. 8.

Burn off the filter paper at a *dull red*-heat and weigh the $BaCO_3$. The weight multiplied by 0.0608 gives the carbon.

To determine the carbon by titration proceed as follows: Put the filter paper and contents in a small flask, add an excess of N/10 HCl, and shake the flask to open the paper, add a few drops of methyl orange solution and titrate the excess of acid with N/10 NaOH. The difference between the amounts of N/10 acid and alkali used multiplied by 0.0006 gram gives the carbon.

See page 28 for direction for preparation of N/10 HCl and N/10 NaOH.

Instead of using a chemical indicator for the end point, the carbon may be exceedingly accurately determined by the electrometric method, measuring the change in resistance of the solution as the $Ba(OH)_2$ is precipitated from solution as $BaCO_3$. (See CAIN and MAXWELL, *Tech. Paper* 141, U. S. Bureau of Standards.)

Notes.—One hundred and fifty cubic centimeters of wash water will dissolve about 0.0003 gram of $BaCO_3$ = 0.000018 gram of carbon. This would be negligible for most purposes, and the amount dissolved would be really less than this because of the repression of solubility during the first washings by the barium hydroxide still present; also, it is quite possible that in the rapid passage through the filter there has not been sufficient time for the wash water to become saturated with barium carbonate.

When using this method the calcium chloride or phosphorus pentoxide in the purifying and absorbing trains is not necessary.

When working with steels high in carbon (above 1 per cent) it is advisable not to use more than 1 gram, in order that filtration may be sufficiently rapid. For very accurate work the Meyer tubes should be washed with dilute acid before beginning work each day. After a determination is finished, the Meyer tube should be completely filled two or three times with tap water, then rinsed with distilled water, in order to remove the carbon dioxide liberated when dissolving the carbonate from the previous determination.

The flask containing the carbonate should be very thoroughly agitated after adding the acid, since the carbonate sometimes dissolves rather slowly if this is not done; this is particularly the case if it has packed much during filtration.

The rubber tube connecting *B* (see Fig. 8) to the Meyer tube should be washed with a little water from *B*, before beginning determinations each day.

REFERENCE:

CAIN, *J. Ind. Eng. Chem.*, 6 (1914), 465.

Other Direct Combustion Processes.—For alloys, F. Wüst mixes the sample with five times it weight of a powdered alloy composed of three parts of tin and one part of antimony and ignites in a current of oxygen at 900°C. Combustion is complete in 10 minutes. (*Metallurgie*, **7**, p. 321.)

DeNolly and Queneau burn the sample of steel in a flask. The sample is suspended in a boat in the flask and is ignited by means of electricity applied by means of a pair of electrodes which touch the drillings. A current of oxygen is directed on the drillings until combustion is complete. The CO_2 is absorbed in a known volume of standard alkali which is titrated after the flask is cool. Sulfur is said not to interfere. Time required is five to seven minutes. (See DENOLLY, *Chimiste*, **3**, 26; QUENEAU, *Met. Chem. Eng.*, **9**, 441.)

Mahler and Goutal employ a bomb and burn the sample in oxygen at eight atmospheres pressure. The drillings are fired electrically by means of a fine wire as in calorimetry. The gas is passed through $Ba(OH)_2$, which is titrated with oxalic acid. (*Compt. rend.*, **153**, 549.)

THE DETERMINATION OF CARBON IN PIG IRON AND STEEL INVOLVING SEPARATION OF THE CARBON FROM IRON

Not many years ago this method was widely used but it has been displaced by direct combustion. It is now used only for special work, and, therefore, will not be described in detail.

When a sample of iron is dissolved in a strong solution of K_2CuCl_4, all of the carbon in the sample is left undissolved, whether it be present as graphite, combined as Fe_3C or in solid solution as austenite. The reactions may be represented as follows:

$$Fe + K_2CuCl_4 = FeCl_2 + Cu + 2KCl$$

and

$$Fe_3C + 3K_2CuCl_4 = 3FeCl_2 + 3Cu + C + 6KCl.$$

The copper then redissolves as follows:

$$K_2CuCl_4 + Cu = 2KCuCl_2.$$

The carbon liberated can be filtered off and ignited to CO_2 by either wet or dry oxidation.

It is essential that there be no hydrogen liberated during the solution of the iron, or hydrocarbons will be liberated, causing loss of carbon. The method cannot be used on some alloy steels or ferro-alloys because of such loss of carbon. According to Moore and Bain (*J. Soc. Chem. Ind.*, **27**, 845), when steel is dissolved in K_2CuCl_4, there is a slight loss of carbon or hydrocarbon. The higher the percentage of carbon in solid solution, the greater seems to be the loss. Thus, the loss is greater on a hardened steel than on the same steel after annealing. (DILNER, *J. Iron Steel Inst.*, **11** (1904), 255.)

The carbonaceous residue often contains some silica and phosphide of iron and sulfide of copper. Alloy steels may also give a residue of tungsten, chromium, vanadium and molybdenum.

The KCl serves to hold the cuprous salt in solution and greatly hastens the action.

This solution has a tendency to dissolve organic matter, which is liable to be subsequently precipitated with the carbon in the steel. This is especially true of the ammonium salt, it being very difficult to obtain it free from organic matter (derived from the ammonium salts used in its manufacture). The salt should be thoroughly purified by recrystallization. The potassium salt is more easily obtained free from this contamination, and for this reason is to be preferred.

A large excess of the solution is required to prevent separation of metallic copper with the carbon.

THE DETERMINATION OF CARBON IN STEEL BY COLOR

This method has been in general use in steel works, but is almost displaced by the direct combustion method. It depends upon the fact that when steel is dissolved in dilute HNO_3 a brown compound containing the carbon forms. This goes into solution, on boiling, coloring the liquid more deeply as the percentage of carbon is higher. Pure iron dissolves in HNO_3 (sp. gr. 1.2) giving a nearly colorless solution, from which every trace of color is removed by moderate dilution.

The color produced by the carbonaceous matter is rapidly altered by light. Its depth depends somewhat on the mode of solution, the concentration of the acid and the kind of steel, hence the process must be conducted strictly according to rule to get concordant results.

There is required: First, a standard steel, which must be of exactly the same kind as that to be tested, and also similar in its composition and of approximately the same carbon percentage. The carbon in this must have been accurately determined gravimetrically. Second, nitric acid of sp. gr. 1.2, perfectly free from chlorine, the least trace of which will seriously alter the color of the iron solution, making it more yellow. The above strength corresponds to one volume of concentrated acid to one volume of water. Third, comparison tubes of clear white glass, graduated in $\frac{1}{10}$ c.c., and of exactly equal diameters.

For comparing the colors an arrangement such as is shown in Fig. 9 is convenient. It consists of a wooden box open at one end and closed by a sheet of ground glass at the other. The glass is covered with black paper, except the two slits *A*, before which the tubes are placed and compared by the observer, who looks into the large end of the box. The tubes are carried by a little rack *B*, which can be revolved by turning the knob *C*, and the tubes thus reversed without taking them out of the box. This reversal of the tubes is important, as the eye will usually see the right-hand tube darker. In the absence of such a "camera," a piece of wet paper on a window makes a good temporary background. Many kinds of colorimeters are on the market.

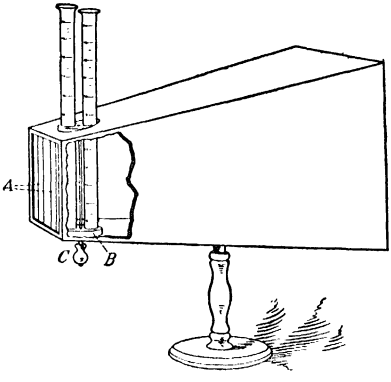

FIG. 9.

If the steel contains much sulfur, the solution will be slightly *turbid* from free S. Comparison is difficult in this case.

The volume of acid used should bear some relation to the percentage of carbon present. The amount of metal taken must be increased when the carbon is low. It is essential that both standard and sample be treated exactly alike, as to the amount of sample taken, time of heating and volume of acid. It is especially important that the standard and the sample should have undergone the same "heat-treatment" in their manufacture. Only the combined carbon is determined by the color method, any free carbon present not affecting the color.

Process of Analysis.—Weigh 0.2 gram of the steel and of the standard, each into a 6-in. test-tube. Add to each tube a measured volume of cold HNO_3 (sp. gr. 1.2) using the following amount: for steels with not over $\frac{3}{10}$ per cent carbon, 4 c.c.; from $\frac{3}{10}$ to $\frac{5}{10}$ per cent, 6 c.c.; from $\frac{5}{10}$ to 1 per cent, 8 c.c.; and over 1 per cent, 10 c.c.

Stand the tubes in cold water till violent action ceases. Then set them in boiling water and heat until the solution is perfectly clear and no more fine bubbles of gas appear. Keep the mouths of the test-tubes closed loosely by little glass bulbs or balls to prevent drying of the iron salts on the sides of the tubes. The time required will be from 15 to 30 minutes, according to the percentage of carbon in the steel. Now cool the tubes in water. Add an equal volume of water to each and pour into the comparison tubes. Dilute carefully until the colors match. The percentages of the carbon will be to each other as the volumes of the liquids in the tubes.

Where a number of steels are to be tested at once, it is convenient to dilute the standard until each cubic centimeter represents some definite percentage of carbon, and then match it with the others, so that the readings in cubic centimeters can be readily converted to per cents. For example, if the standard contained 0.38 per cent carbon, dilute it to 19 c.c., then if a comparison showed the unknown steel to read 16 c.c. it would obviously contain 0.32 per cent carbon.

Where the color carbon process is used on steels of comparatively uniform contents, it is usual to take 10 c.c. of acid and then enough of the sample to give a sufficiently marked color with this amount; for example, 0.5 gram of steel and 10 c.c. of acid. In the case of very low-carbon steel (under 0.2 per cent), 1 gram of steel may be dissolved in 20 c.c. of acid.

Notes on the Process.—The color process can be applied to pig iron and gives an approximate determination of its combined carbon. In this case a solution of the sample and of the standard must each be filtered through a small filter and the solutions compared. Filters of the same size and a pig iron standard must be used.

The use of permanent standard colors, either organic or inorganic, such as the mixed chlorides of iron, copper and cobalt, has been tried. This is not advisable, as it does not provide for the variations in color due to slight differences in the treatment, as well as does the treatment of standard and sample together. (For these methods see *Trans.* Am. Inst. Min. Eng., **1,** 240; **16,** 111.)

For very low-carbon steels the color is faint and uncertain. An alkaline method has been used on such metals. (See STEAD, *J. Iron Steel Inst.* (1883), No. 1, 213.)

THE DETERMINATION OF THE GRAPHITE IN PIG IRON

When pig iron is boiled with HCl or dilute HNO_3 the combined carbon is converted into solid, liquid or gaseous hydrocarbons or nitro compounds, while the graphite is all left insoluble. The non-volatile hydrocarbons are soluble either in alkalies, in alcohol or in ether. The graphite or uncombined carbon is not acted upon by any of these reagents but remains in the residue as a black mass. The residue may also contain hydrated silica and frequently titanium carbide and free sulfur. The silica holds water tenaciously and cannot be thoroughly dehydrated below a red-heat. Titanium carbide is decomposed by HNO_3, but not by HCl; while sulfur is separated by dilute HNO_3, but not by HCl. Graphite is not at all oxidized by HNO_3 (sp. gr. 1.2). The use of nitric acid is preferable with gray irons low in combined carbon, while HCl is better for white iron high in combined carbon and for ferro-silicons, as these only dissolve with difficulty in HNO_3. The carbon in in the residue can only be accurately determined by combustion.

REFERENCES:

SHIMER, *J. Am. Chem. Soc.*, **17**, 873.
DROWN, *Trans.* Am. Inst. Min. Eng., **3**, 41.

Process of Analysis.—Treat 2 grams of drillings in a beaker with 50 c.c. of HCl (sp. gr. 1.12). Cover and boil briskly for 30 minutes. Dilute, filter on an asbestos filter and wash with hot water until all iron salts are removed. Then pour on a little HCl and wash again with water. Now wash the residue with a 30 per cent solution of caustic soda, then with water, then with alcohol, then with ether, and finally with cold water and then hot water till every trace of ether is extracted. Now transfer to the carbon apparatus and determine the carbon with chromic acid and sulfuric acid, or by combustion in oxygen.

This complicated washing is required to remove the solid and liquid hydrocarbons which are likely to form and are insoluble in water alone.

The ether must be followed by cold water; if hot water were added at once, it would make the ether boil and might throw the carbon out of the filter tube. Nitric acid of sp. gr. 1.135 can be substituted for HCl with such irons as are readily dissolved by it. If a little HF is added to the solution after the metal is dissolved, it will frequently greatly facilitate the filtration by preventing the separation of silica in a gelatinous form. By using a sufficient quantity of acid of the right specific gravity, most of the silica will usually remain in solution.

DETERMINATION OF THE GRAPHITE BY DIRECT WEIGHING

This method gives satisfactory results on many irons. It is quite generally used as a rapid method. It should be checked by the combustion method when applied to kinds of iron not previously tested.

The residue is dried at 100°C. and then burned and the loss of weight assumed to be carbon. Any sulfur or water which the residue contains will, of course, be rated as carbon.

Process.—Weigh out 2 grams of the drillings into a 250-c.c. beaker. Add 100 c.c. of HCl (sp. gr. 1.1), or of HNO_3 (sp. gr. 1.135). Boil gently till all action ceases. Keep the beaker covered to prevent evaporation and concentration of the solution which may cause the separation of silica. Finally add 3 or 4 drops of HF and boil again. Prepare a Gooch perforated crucible as follows: First, heat, cool and weigh it; second, fit into the bottom of the crucible a disc of ashless filter paper and dry the paper and crucible at 100° for 20 minutes and weigh again. Filter the solution through this crucible in the ordinary way, transferring the residue with cold water. Then wash the residue with hot dilute HCl, then with hot water and then with a 5 per cent solution of NH_4OH. When the filtrate runs through colorless, finally wash with a mixture of equal parts of alcohol and ether. Now dry the crucible and contents at 100°C. to constant weight, which will take from 10 to 20 minutes. Now set the crucible over a Bunsen burner flame and burn off the residue. When all the carbon has burned away, weigh the crucible again.

By subtracting the weight of the crucible with the filter paper from the weight of the crucible plus the filter paper plus the residue, the weight of the residue is obtained. Subtracting the weight of the empty crucible from the final weight of the crucible plus the incombustible portion of the residue gives the silica and other mineral matter with the carbon. Subtracting this remainder from the total weight of the carbonaceous residue gives the weight of the graphite. A still better way is to use an asbestos mat in the Gooch crucible.

Instead of using a Gooch crucible, two small tared filters can be taken and the residue then burned out in an ordinary crucible, but this is not nearly so convenient.

The above method is essentially that given by A. B. Harrison in "Methods of Iron Analysis Used around Pittsburgh," 2nd ed., p. 85.

REFERENCES:

For variations of the method and discussion of the results consult:
DAUGHERTY, *Chem. News*, Sept. 8, 1899.
CROBAUGH, *J. Am. Chem. Soc.* (1894), 104.
AUCHY, *J. Am. Chem. Soc.* (1900), 47.

CHAPTER IX

THE DETERMINATION OF NICKEL AND COBALT IN STEEL

The method for nickel here given is that of Moore, modified by Johnson. It is very rapid and accurate and no elements interfere except copper and cobalt, which are usually present in steel in very small amounts. The copper reacts like nickel and, if present in more than traces must be separated as directed on pages 154, 126.

The method depends upon the following reaction:

$$Ni(NH_3)_6SO_4 + 4KCN = K_2Ni(CN)_4 + K_2SO_4 + 6NH_3.$$

This reaction takes place in a solution slightly alkaline (with ammonia) and a very large amount of iron may be present without interfering, if, before making alkaline, a large amount of citric acid is added. The citric acid combines with the iron to form un-ionized iron citrate which does not allow the iron to precipitate when the ammonia is added.

The end point of the reaction between the nickel and the cyanide is shown by the disappearance of a turbidity due to the presence of silver iodide. The reaction is:

$$AgI + 2KCN = KAg(CN)_2 + KI.$$

Copper can be separated from nickel easily by the use of H_2S, but cobalt is not so easily separated. Nickel can be quantitatively separated from small amounts of cobalt by precipitating it with dimethylglyoxime and cobalt can be separated from nickel by precipitating the cobalt with nitroso-β-napthol. Nickel and cobalt along with vanadium, copper, manganese and aluminium can be separated from iron by extracting the chlorides with ether, only a small amount of iron remaining with the nickel, etc. (See page 125.)

For rapid routine determinations of nickel the cyanide titration method is recommended, but for the most accurate results the dimethylglyoxime should be used.

Cyanide Titration Method.—Dissolve 1 gram of steel drillings in a 150-c.c. beaker with 20 c.c. of 1:1 HCl. When action ceases add 10 c.c. of 1:1 HNO_3.

Reduce the volume to 15 c.c., remove the beaker from the heat and pour into it 8 c.c. of sulfuric acid diluted with 25 c.c. of water. Transfer the contents of the beaker to a 400-c.c. beaker containing 12 grams of powdered citric acid and stir until it is all dissolved. Make the solution faintly but distinctly alkaline with 1:1 NH_4OH. Do not add much excess as it causes low results. Cool the solution and dilute to about 300 c.c. If it is turbid, filter it.

Add to the cold solution 2 c.c. of 20 per cent solution of potassium iodide and then run in from a burette a standard solution of silver nitrate, with stirring, until a distinct turbidity due to silver iodide is produced. Then titrate with the standard cyanide. Run in the cyanide with constant stirring until the turbidity just disappears. The cyanide first reacts with the nickel then attacks the iodide. If it is thought that the end point is passed, add another measured amount of silver nitrate until a turbidity is formed and again titrate with the cyanide until the turbidity just disappears. It is best to have another beaker containing a solution to be titrated to which no silver nitrate has been added sitting beside the one being titrated, so as to have a clear solution of the same color to compare with. If the citric acid was dirty, the solutions will be cloudy and should be filtered before the silver nitrate is added.

Standardization of the Solutions.—Dissolve about 5 grams of KCN and 1 gram of KOH in water and dilute to 1 liter. The KOH makes the KCN solution keep better. Also dissolve 2.900 grams of $AgNO_3$ in water and dilute to 500 c.c. One cubic centimeter of each will be equal to about 0.001 gram of nickel. To standardize them, weigh out 1 gram of nickel-free steel and add 0.3370 gram of $NiSO_4(NH_4)_2SO_46H_2O$, which contains 14.85 per cent of nickel, and treat just as above directed for a nickel steel up to the point of titration. Make the titration carefully until the turbidity just disappears. Now add 10 c.c. of the cyanide in excess and titrate with the silver nitrate until a turbidity just appears. This second titration gives the relation between the silver nitrate solution and the cyanide solution. For example, suppose that in the first place 0.5 c.c. of silver solution was added and 50.5 c.c. of cyanide were used. Then suppose that it took 10.8 c.c. of silver nitrate solution to produce a turbidity after the 10 c.c. of extra cyanide were added. The cyanide required to titrate the nickel would be $50.5 - 0.5 \times \frac{10}{10.8} = 50.04$ c.c. Since the amount of nickel present was 0.3370×0.1485, or 0.050 gram, the strength of the cyanide is $0.050 \div 50.04 =$ 0.0009992 gram Ni per cubic centimeter.

Notes on the Process.—The presence of sulfates is necessary to obtain a sharp end reaction. Silver iodide is soluble in a large excess of NH_4OH, so care should be taken to have the solution only slightly alkaline with NH_4OH, but it must be alkaline.

If the titrated solutions are allowed to remain in the open beakers for some time a white film forms on the surface, but no account is to be taken of it.

When chromium is present, proceed exactly as described above, except add 24 grams of citric acid. Instead of using so much citric acid, some chemists use citric acid and sodium pyrophosphate.

The silver nitrate solution used should not be stronger than that indicated above, for when a strong silver solution is used, the silver iodide, instead of forming a turbid solution, settles out as a curdy precipitate which does not readily react with the cyanide. If a ferronickel is being analyzed, a stronger solution of KCN should be used.

Such elements as vanadium, chromium, tungsten, molybdenum or manganese do not interfere, even when present in large amounts in the sample.

REFERENCES:

JOHNSON, "Chemical Analysis of Special Steels, Alloys and Graphites."

GROSSMAN, *Chem. Ztg.*, **36,** 673.

JAMIESON, *J. Am. Chem. Soc.*, **32,** 757.

BOYLE, *Chem. Eng.*, **14,** 288.

DAUGHERTY, *Chem. News*, 95–261.

THE DIMETHYLGLYOXIME METHOD FOR NICKEL

This is a very accurate and fairly rapid method. Copper and cobalt, if present, do not interfere and for this reason steels containing more than traces of copper or cobalt should be analyzed by this method. In cases of dispute, umpire analyses should be made in this way.

From faintly ammoniacal solution, dimethylglyoxime precipitates nickel promptly and completely as a voluminous red compound, nickel dimethylglyoxime, which is soluble in acid solutions. The precipitate has the composition $(CH_3)_2C_2(NOH)_2Ni(CH_3)_2C_2(NO)_2$ and when dried at 115°C. contains 20.32 per cent nickel.

For use, the dimethylglyoxime ($CH_3CNOHCNOHCH_3$) is dissolved in alcohol, 1 gram to 100 c.c. Since the precipitate is distinctly soluble in a solution containing more than 50 per cent of alcohol, the volume of the solution to which the alcoholic dimethylglyoxime is added should be greater than that of the alcoholic solution.

Method of Analysis.—Treat the sample exactly as was directed for the cyanide determination of nickel until the ammonia is added to the solution containing citric acid. As soon as the solution becomes alkaline, add acetic acid until it is acid and then heat to boiling. Now add about 20 c.c. of the dimethylglyoxime solution, or five times as much dimethylglyoxime as there is nickel present. Then add ammonia until the solution smells slightly of ammonia or reacts alkaline. While still hot, filter on a weighed Gooch crucible, wash well, dry at 110 to 120°C. for 45 minutes and weigh. Multiply the weight by 0.2032 to get the weight of the nickel.

Notes on the Process.—The nickel dimethylglyoxime sublimes at 250°C., hence it should not be heated too long and too hot.

In the precipitation large amounts of ammonium salts do no harm, but an excess of ammonia tends to prevent the formation of the precipitate.

If cobalt be present in considerable amount, the solution should be diluted to 100 c.c. for every 0.10 gram of cobalt.

The dimethylglyoxime method, when properly modified to suit the samples, makes an excellent method to determine the nickel in ores.

The reagent is expensive. It may be recovered by mixing the nickel salt to a paste with water, warming with potassium cyanide, filtering hot and precipitating the oxime with acetic acid.

High-silicon steels should have the silicon removed before precipitating the nickel. If the nickel content is less than 0.100 per cent, it is best to carry out the ether separation for nickel as given on page 125.

When the nickel is low in amount, under 0.2 per cent, the precipitate settles slowly and should be allowed to stand several hours before filtering.

When the sample contains cobalt, an excess of 10 c.c. of ammonia is added, then 10 c.c. of a 10 per cent solution of sodium chlorate and the solution boiled for five minutes, then nitric acid is added until only faintly alkaline and the precipitation made as usual.

When tungsten is present in small amounts it does not interfere, if present in large amounts it should be removed as described under tungsten.

Instead of weighing the nickel dimethylglyoxime, the precipitate may be dissolved in nitric acid, the solution boiled for five minutes and the nickel then determined by titration by the cyanide method as previously described.

References:

Brunk, *Z. angew. Chem.*, **20**, 834.
Ibbotson, *Chem. News*, **104**, 224.
Parr and Lindgren, *Trans.* Am. Brass Founders Assoc., **5**, 120, describe a method for titrating the nickel dimethylglyoxime.
Kelley and Conant, *J. Ind. Eng. Chem.*, **8**, 804.

The Determination of Cobalt in Steel

Cobalt is present to some extent in all samples of iron and steel that contain nickel. It is now being intentionally introduced into some varieties of high-speed steel, and in stainless steels.

Cobalt is separated from most of the iron in a hydrochloric acid solution by means of the ether separation, along with nickel, manganese, copper, vanadium, aluminium and chromium. In this solution the nickel and cobalt are separated from the other elements by means of hydrogen sulfide. If cobalt is present in small amounts it is best separated from the nickel by Ilinsky and Knorre's reagent (nitroso-β-naphthol). If present in large amounts it is best to deposit the cobalt and nickel together electrolytically or weigh as sulfate and then dissolve the deposit and precipitate the nickel with dimethylglyoxime.

Process of Analysis.—Dissolve 1 to 5 grams of the sample in 30 c.c. of HCl (sp. gr. 1.1). When dissolved add a few drops of HF, warm and add gradually 1 or 2 c.c. of HNO_3 to oxidize the iron. Add ½ gram of sodium chlorate and boil until any metallic residue is dissolved or tungsten, if present, is a clean yellow. Filter off any WO_3 that may have been formed and wash with 10 per cent HCl until all iron is removed. Add 3 c.c. of HNO_3 and evaporate to a volume of 40 c.c. Cool and transfer to a separatory funnel with the aid of 1.11 sp. gr. HCl. The total volume should not exceed 50 c.c. Then 40 c.c. of ether are added to the beaker and transferred to the funnel, which is stoppered and vigorously shaken. Allow the ethereal solution to separate from the aqueous solution. Most of the iron remains in the ethereal solution. Draw off the aqueous solution into a beaker, add 3 c.c. more of HCl (sp. gr. 1.11) and shake again, finally drawing off the small amount of aqueous solution into the beaker. Heat the solution in the beaker cautiously until the ether is all expelled, add 100 c.c. of 5 per cent citric acid solution, neutralize with ammonia and add 5 c.c. in excess. Dilute to 200 c.c. and saturate with H_2S to precipitate the sulfides of cobalt, nickel, manganese and traces of iron. Filter and wash the precipitate three or four times with H_2S water. Transfer the paper and contents to a crucible, roast carefully at a low temperature and finally ignite at a high temperature for 20 minutes, cool and weigh. Dissolve the oxides in a 250-c.c. beaker with 50 c.c. of HCl, dilute to 150 c.c., neutralize with ammonia, add 10 c.c. excess and ½ gram of ammonium persulfate and boil for a few minutes. Filter the oxides of iron and manganese, wash with water, ignite and weigh. The difference in weight between this weighing and the weight of the total oxides gives the weight of cobalt and nickel oxides.

The filtrate contains the nickel and cobalt. Add to it 1 gram of sodium chlorate and boil for five minutes. Neutralize with nitric acid, then add ammonia and precipitate the nickel with dimethylglyoxime as usual, if the nickel is present in small amounts compared to cobalt. If cobalt is present in small amounts compared to nickel, precipitate the cobalt out with the nitroso-β-naphthol after the solution has been made acid with 10 c.c. excess of HCl, as directed below. The nickel and cobalt were present in the ignited oxides as NiO and Co_3O_4. Calculate the nickel or cobalt obtained by precipitation to the proper oxide, subtract from the sum of NiO and Co_3O_4 and calculate the other metal present.

If copper is present, it should be removed after the ether separation by hydrogen sulfide from the acid solution.

Nitroso-β-naphthol Method for Cobalt.—Dissolve the sample as directed above, evaporate until salts begin to separate, add 3 c.c. of water, transfer to a 500-c.c. flask and cool. Add zinc oxide emulsion in excess as in the Volhard process, dilute to the 500 c.c. mark. Mix well and allow to settle. Filter off 250 c.c., add 5 c.c. of HCl, dilute to 300 c.c., heat to boiling and add 6 c.c. of nitroso-β-naphthol solution for each 0.01 gram of cobalt present.

The cobalt is precipitated as a voluminous red compound with some of the excess reagent. When the precipitate is settled, filter the hot solution and wash with 1:1 HCl several times and finally with hot water until no test for chloride is obtained. Ignite in a porcelain crucible gently at first and finally at a high temperature until all carbon is burned off and the cobalt is present as Co_3O_4. Weigh and multiply the weight by 0.7343.

The cobalt oxide may be dissolved and titrated by the cyanide method as directed for nickel if a check is desired.

Notes on the Process. Nitroso-β-Naphthol Solution.—Dissolve 1 gram of nitroso-β-naphthol in 15 c.c. of glacial acetic acid.

Instead of weighing cobalt as Co_3O_4, some chemists prefer to transform it to the sulfate as directed under manganese on page 80 and weigh as $CoSO_4$ containing 0.3804 cobalt.

Cobalt and nickel may be deposited together electrolytically from a solution of the sulfates containing 30 c.c. of ammonia (sp. gr. 0.9) in excess in 100 c.c., using a gauze cathode and a current of 1 amp.

Nitroso-β-naphthol also precipitates copper, chromium and iron, but does not precipitate aluminium, lead, cadmium, manganese, nickel, mercury and zinc.

The cobalt nitroso-β-naphthol precipitate is very voluminous, hence it is not advisable to precipitate large amounts of cobalt in this way. Its formula is $[C_{10}H_6O(NO)]_3Co$.

The cobalt precipitate may be ignited in a Rose crucible with oxalic acid until all the carbon is burned off and finally reduced to metal by igniting in a current of hydrogen. It is difficult to eliminate all of the carbon.

The nickel may be determined in the filtrate from the cobalt by evaporating with 10 c.c. of H_2SO_4 to destroy the nitroso-β-naphthol and precipitating with dimethylglyoxime or KOH and bromine.

The electrolytic deposit of cobalt is generally brown or black and the results tend to be a trifle high. If too small an amount of NH_4OH is used, some nickel or cobalt oxide may deposit on the anode, while too large an amount retards the deposition of the metals. Nitrates should be absent.

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Funk, *Z. anal. Chem.*, **45** (1906), 562 (sulfide precipitation).
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Copaux, *Chem. News*, **87** (1903), 291 (nitroso-β-naphthol method).
Smith, "Electro-analysis," p. 122.
Mellor, "Quantitative Inorganic Analysis," pp. 389, 394.
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PRECIPITATION OF NICKEL BY ALPHA BENZILDIOXIME

The alcoholic solution of alpha benzildioxime gives an intensely red precipitate of $C_{28}H_{22}N_4O_4Ni$, when added to ammoniacal solutions containing nickel. The reaction is more characteristic for nickel than is that with dimethylglyoxime and is more delicate. In a volume of 5 c.c. (according to F. H. Atack), one part of nickel in two million parts of water may be detected. In the presence of 100 times as much cobalt only a faint yellow color is produced by the cobalt. One part of nickel per million of water will cause precipitation with the compound, whereas no precipitate is formed with dimethylglyoxime under the same conditions. With glyoxime, iron produces a pink color; with alpha benzildioxime, ferrous salts give a faint violet color, hence do not interfere in the detection of nickel. Silver, magnesium, chromium, manganese and zinc do not interfere. Since the nickel precipitate with this reagent is exceedingly voluminous, it is advisable to have not more than 0.025 gram of nickel in the solution in which the nickel is being determined. The method is adapted to the detection and determination of minute traces of the element up to small amounts of less than 10 per cent nickel.

Reagent, Alpha Benzildioxime.—The reagent is prepared by dissolving 0.2 gram of the salt per liter of alcohol, to which is added ammonium hydroxide to make 5 per cent solution (sp. gr. 0.96), (50 c.c. per liter).

Procedure.—Proceed exactly as directed for the dimethylglyoxime method, except that if nitric acid has been used it must all be removed by evaporation with sulfuric acid. The precipitate when dried at 110°C. contains 10.93 per cent nickel.

CHAPTER X

THE DETERMINATION OF VANADIUM IN STEEL, ALLOYS AND ORES

Vanadium is found in small amounts in some steels, such as spring steels, containing about 0.15 per cent and in larger amounts in high-speed steels, containing up to 2 per cent of vanadium. The vanadium is present in the steel largely as a carbide when in small amounts. Other metallurgical materials containing high amounts of vanadium are ferro-vanadium and iron vanadate. Vanadium ores as mined in this country contain an average of about 4 per cent or less of vanadium pentoxide.

Vanadium may be determined gravimetrically or volumetrically. In the gravimetric methods the vanadium is precipitated as lead or mercury vanadate. The volumetric methods depend upon the fact that vanadium exists in solutions in the pentavalent and quadrivalent conditions and, as in the cases of iron, manganese, chromium and other metals with several states of valence in solutions, the amount of vanadium may be determined by measuring the amount of standard oxidizing or reducing solutions required to effect the changes.

Determination of Vanadium in Steels Low in Vanadium.—As stated under the determination of nickel, when a HCl solution of steel containing Mn, Ni, Cr and V is shaken with ether and the two layers are allowed to settle, the iron remains nearly entirely in the ethereal layer on top and the chlorides of these other metals go into the heavier aqueous layer. This enables one to concentrate the vanadium from a large sample of steel or other alloy, leaving only a small amount of iron with the vanadium. This method is very exact and should be used in all important cases.

Satisfactory separation requires that the aqueous solution used must contain HCl sufficient to make a sp. gr. of 1.1 to 1.3 and the volume of the solution must be kept small. The ether must be free from alcohol and should be saturated with HCl.

Process of Analysis.—Dissolve 5 grams of the drillings in 60 c.c. of 1:1 HCl. When action ceases add a few drops of HF, heat and add 3 c.c. of HNO_3 and evaporate to about 25 c.c., transfer the solution to a small separatory funnel and wash the beaker with HCl of 1.11 sp. gr., taking care to keep the total volume of the solution under 50 c.c. Add an equal volume of ether previously saturated with HCl and shake vigorously, taking care that the heat of the hand does not cause the ether vapors to blow out the stopper. Allow the two layers to separate clear from each other and draw off the lower aqueous solution. Add 2 c.c. of 1.11 sp. gr. HCl and a few drops of H_2O_2 to the separatory funnel and again shake, allow the solution to settle and draw off the aqueous solution into the beaker containing the first extract.

Carefully heat the aqueous solution until all the ether is expelled, add 20 c.c. of 50 per cent H_2SO_4 and evaporate until fumes of SO_3 are given off copiously. Cool, add 5 c.c. of 4 per cent $KMnO_4$ and heat to destroy all carbonaceous matter. Add 30 c.c. of HCl and again evaporate to fumes of SO_3. Cool the solution, add 100 c.c. of water and titrate at 40°C. with a standard N/10 permanganate solution until a faint pink color is obtained which persists for one-half minute. Each cubic centimeter of the decinormal permanganate oxidizes 0.0051 gram of vanadium. The end point may be obtained electrometrically. (See page 252.)

The determination as above described depends upon the reduction of any pentavalent vanadium by HCl in hot concentrated H_2SO_4, under which conditions ferric iron is not reduced to ferrous iron. The permanganate then oxidizes the quadrivalent to pentavalent vanadium by the reaction.

$$5V_2O_2(SO_4)_2 + 2KMnO_4 + 22H_2O = 10H_3VO_4 + K_2SO_4 + 2MnSO_4 + 7H_2SO_4.$$

When the sample contains tungsten, the tungsten must first be removed as directed for the determination of tungsten and the filtrate from the WO_3 prepared for the ether separation as above directed.

Determination of Chromium.—The solution which has been titrated for vanadium as above directed has all the chromium which the sample contained, and the chromium may be accurately determined by adding 5 c.c. of HNO_3, 5 c.c. of phosphoric acid and oxidation of the chromium followed by titration as directed on page 135.

Ferrous Sulfate Method for Vanadium.—Dissolve 2 grams of steel in 20 c.c. of 1:1 H_2SO_4 and 60 c.c. of water. When effervescence slows down add 5 c.c. of HNO_3 and 1 c.c. of HCl and boil it for 10 minutes, cool, dilute to 100 c.c. and filter. To the filtrate add 5 c.c. of H_3PO_4 and then strong potassium permanganate solution until a permanent pink color is obtained. Add standard ferrous sulfate solution (0.05 normal) until the yellow color of chromic and vanadic acids is discharged, then add 10 c.c. more, stir thoroughly, add 8 c.c. of a 15 per cent ammonium persulfate solution and stir vigorously for one minute. Titrate with a decinormal permanganate solution until a pink color is obtained which remains for one minute.

Notes on the Process.—The phosphoric acid is used to decrease the yellow color due to iron. In the presence of much chromium the color of the solution is a dark green, which makes the permanganate end point difficult to see. This makes it essential that blank determinations be made on steels containing no vanadium but approximately the same amount of chromium as the sample being analyzed. The correction amounts to about 2 per cent of the chromium present. Thus a steel containing 1.5 per cent Cr would make necessary a blank of 0.03 per cent to be subtracted from the results for vanadium. Electrometric titration makes this correction unnecessary. (See page 252.)

After the titration following HCl reduction as given on page 130 has been made, the results may be checked by adding 5 c.c. of HNO_3 boiling several minutes, cooling, reducing with ferrous sulfate, reoxidizing with persulfate and titrating as directed above.

The ammonium persulfate is used to oxidize all the ferrous iron present, at the same time the vanadium is unaffected.

It is essential when titrating vanadium with permanganate that the pink end point persists for at least one minute, as vanadium oxidizes slowly with permanganate.

After the permanganate titration has been finished the vanadium can be again titrated by adding 1 c.c. of a 0.1 per cent $K_3Fe(CN)_6$ solution and very carefully adding a 0.05 normal solution of ferrous sulfate until a drop produces a green color in the solution.

Process for Ferrovanadium.—Dissolve ½ gram of the pulverized sample in a platinum dish with a mixture of 30 c.c. of water, 30 c.c. of 1:1 HNO_3 and 20 c.c. of 1:1 H_2SO_4, adding a few drops of HF occasionally until the alloy is completely decomposed and evaporate until copious fumes of SO_3 are liberated. Cool, add 20 c.c. of water and transfer to a flask, dilute to 400 c.c., add 15 c.c. of 1:1 H_2SO_4, cool, add $KMnO_4$ solution until a faint pink color is obtained. Add a decinormal solution of ferrous sulfate until a drop tested on a white plate with potassium ferricyanide indicator shows the presence of ferrous iron, then add 5 c.c. excess of the ferrous solution and stir for a minute. Now add 8 c.c. of 15 per cent ammonium persulfate and stir for one minute to reoxidize all iron. Titrate slowly with a decinormal solution of potassium permanganate until a faint pink color is obtained which persists for one minute. If the iron value of the permanganate is known, its iron value multiplied by 0.914 gives its vanadium value.

Instead of reducing with ferrous sulfate, the HCl method as given on page 130 may be used.

Chrome ores and brick may be analyzed in exactly the same way as ferrovanadium, except that the ore must first be decomposed by prolonged fusion with $KHSO_4$ or by fusion with Na_2CO_3.

Determination of Vanadium in Materials Insoluble in Acids.—Fuse 1 gram of the material with 10 times its weight of sodium carbonate and 1 gram of sodium nitrate. When fusion is complete, cool, disintegrate with water, filter and wash the residue 15 times with hot water. If the material is high in vanadium, the residue should be fused again with a smaller amount of sodium carbonate and the extraction repeated. The vanadium is in the filtrate with phosphorus, chromium, manganese and similar acid-forming metals.

Gravimetric Method.—The extractions from the fusions as obtained above contain all the vanadium as vanadate. If the solution is colored green by manganate, reduce the latter by adding sodium peroxide in very small amounts. Very carefully add 1:2 HNO_3 from which all nitrous acid has been removed by a current of air, adding the acid drop by drop until the solution is nearly, but not quite, neutral. It is essential that the solution be not allowed to become acid. Add mercurous nitrate solution and about 0.10 gram of mercurous carbonate, heat short of boiling and filter, wash the precipitate with mercurous nitrate solution (neutral). Ignite the filter and precipitate cautiously until carbon is burned off, then raise the temperature to a bright red.

The residue contains all the vanadium, phosphorus, arsenic and chromium as oxides. The separation of chromium and vanadium is too tedious to justify further gravimetric methods, hence the ignited oxides should be dissolved and the vanadium and chromium determined volumetrically. It would not be satisfactory to determine them volumetrically in the solutions resulting from the fusions because the presence of such a large amount of salts makes the titration inaccurate. For gravimetric determination and separation of V and Cr see Briers, *Stahl U. Eisen*, 42-775.

Qualitative Tests for Vanadium (and Titanium).—The color of the phosphomolybdate dissolved in strong sulfuric acid, according to Cain and Hostetter, affords a good qualitative indication of the presence or absence of vanadium. The following test, elaborated by Johnson, also is good. It depends upon the fact that in dilute acid solutions hydrogen peroxide produces a brick-red color with vanadium, due to the formation of pervanadic acid. Titanium under the same conditions causes a yellow color when the peroxide is added. If both vanadium and titanium are present, a mixed color is obtained. If a clear yellow is obtained on adding the peroxide, only titanium is present; but if a reddish color is obtained, both may be present. If ferrous sulfate is added to the solution after the hydrogen peroxide, the reddish color of the vanadium disappears first, leaving the yellow of the titanium.

Procedure.—Dissolve 0.5 gram of the sample in 10 c.c. of 1:3 sulfuric acid, heating until action ceases. Add 5 c.c. of concentrated nitric acid and boil until red fumes are all gone. If tungsten be present, filter. Pour half of the solution into each one of two 6-in. test-tubes. Then add to one tube 5 c.c. of water and to the other 5 c.c. of a 3 per cent solution of hydrogen peroxide. If vanadium be present, the tube to which the peroxide was added will be distinctly redder than the other, even if there be only a few hundredths per cent of vanadium in the sample. If titanium but no vanadium be present, the color will be a clear yellow. If a red color is produced, vanadium, and possibly titanium, is present. Add N/20 ferrous sulfate, 1 c.c. at a time, shaking after each addition, until red color gradually fades. If titanium be present, the red will change to a clear yellow. If none be present, the red will gradually fade out without changing to yellow.

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CHAPTER XI

DETERMINATION OF CHROMIUM IN STEELS AND ALLOYS

Chromium is present in steels largely as carbide of chromium unless the chromium is in large amount. Usually the chromium is not much over 1 per cent of the steel, although in special steels, such as high-speed steel, it may go up to 5 per cent or more. Other alloys containing large amounts of chromium are the resistance alloys, such as nichrome.

The determination of chromium is almost always accomplished volumetrically. Chromium exists in solutions as the trivalent and hexavalent compounds. The measurement of the amount of chromium in solution is very accurately and easily accomplished by determining the amount of a standard reducing solution, usually ferrous sulfate, which is required to reduce the chromium from hexa- to trivalent condition.

Process for Chrome Steels.—Dissolve 2 grams of the drillings in 60 c.c. of a solution containing 35 c.c. of water, 8 c.c. of H_2SO_4 and 2 c.c. of phosphoric acid, heat until effervescence nearly ceases, add 5 c.c. of HNO_3 and boil until solution is complete and fumes of oxides of nitrogen are expelled. If any residue of WO_3 appears, filter it and wash thoroughly with dilute nitric acid. Add silver nitrate solution containing 0.2 gram of silver nitrate for each per cent of chromium present, dilute to 300 c.c., heat to boiling and add 8 c.c. of a 15 per cent ammonium persulfate solution. When the permanganate color is well developed add 2 c.c. of 1:1 HCl and boil until the pink color disappears and the persulfate is decomposed, usually about 10 minutes. (Instead of oxidizing with persulfate in the presence of silver nitrate, it is satisfactory to add a 4 per cent $KMnO_4$ solution to the boiling solution until the permanganate color persists on boiling five minutes and MnO_2 precipitates. Then add 2 c.c. of 1:1 HCl and boil until the precipitate is dissolved and all chlorine expelled.) Cool, dilute to 400 c.c. and titrate the chromium as follows: Add decinormal ferrous sulfate solution until all the yellow tints disappear, indicating complete reduction of chromic and vanadic acids. Add 10 c.c. more of ferrous sulfate and then titrate with decinormal permanganate until a faint pink is obtained which persists for one minute with continued stirring. If vanadium is present, the end point comes slowly, owing to the slow reoxidation of vanadium. In this case it is best to add the permanganate until a strong pink color is obtained, then nearly to discharge the pink by carefully adding decinormal sodium arsenite.

After the end of the titration of chromium the vanadium may be determined by the addition of ferrous sulfate and proceeding as under vanadium. A blank determination should be run to determine the amount of permanganate required to give a visible end point in the solution. If the electrometric end point is used, the end of the titration is sharper. (See page 252.)

The Analysis of Ferrochrome.—Ferrochromium is insoluble in acid, hence must be fused. Proceed as follows: Fuse 0.50 gram of the powdered sample with 7 grams of sodium peroxide in a nickel crucible, maintaining the fusion liquid for several minutes. Cool and disintegrate in a beaker with 300 c.c. of hot water until no hard lumps remain. Acidify with 50 c.c. of 1:1 H_2SO_4, add 2 c.c. of 1:1 HCl and boil until all permanganic acid is destroyed and the liberated chlorine expelled, cool and add decinormal ferrous sulfate until the yellow color of chromic acid is completely discharged and 10 c.c. in excess. Titrate the excess of ferrous sulfate with decinormal permanganate until a pink color is obtained which persists for one minute with stirring.

Add to a beaker containing 300 c.c. of water and 50 c.c. of 1:1 H_2SO_4 the same amount of ferrous sulfate as used in the preceding titration, and titrate. The difference between the permanganate used in the two titrations is the permanganate equivalent to the chromium present.

If the permanganate used is exactly decinormal, the chromium equivalent to 1 c.c. of permanganate is 0.001733. If the iron value of the permanganate has been obtained by standardization against iron, as directed on page 37, the chromium value of the permanganate per cubic centimeter is obtained by multiplying the iron value by 0.310.

The addition of ferrous sulfate reduces both vanadic and chromic acids, but when the reduced solution is titrated with permanganate the end point comes after the vanadium has been reoxidized to its pentavalent form, hence, in effect, the vanadium has no influence on the amount of ferrous sulfate and permanganate required for the titration.

Notes on the Process.—The phosphoric acid is used to hold tungsten in solution; it also decreases the depth of the color in the solution.

If chromium is present in the sample in very small amounts, at least 5 grams of sample should be used and the ether method of separating chromium, vanadium, etc. from iron used, as directed on page 129. The same conditions of solution are then produced as directed above and the chromium titrated as usual.

Instead of using ammonium persulfate or potassium permanganate for oxidizing chromium to chromic acid, sodium bismuthate may be used in place of the permanganate and the process carried on exactly the same.

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CHAPTER XII

THE DETERMINATION OF TUNGSTEN AND SILICON IN STEEL

Tungsten may be found in steel in amounts up to 25 per cent and is generally accompanied by chromium up to as high as 6 per cent.

When a steel containing tungsten is dissolved in a mixture of nitric and hydrochloric acids and the solution is evaporated to dryness and the residue treated with hydrochloric acid, the tungsten is left insoluble as WO_3 with the SiO_2. In order to render the WO_3 entirely insoluble, more than one evaporation to dryness is necessary. When the residue is treated with sulfuric and hydrofluoric acids the silica is driven off while the tungstic anhydride is left behind. The tungstic anhydride is always contaminated with ferric oxide and must be purified for perfect results. The chromium in the filtrate is oxidized to chromic acid and titrated with ferrous sulfate.

The tungsten is usually and best determined gravimetrically by weighing as WO_3, but, since the WO_3 is an acid anhydride, it may be determined volumetrically by titrating with a standard alkali solution.

Tungsten steels are very hard and difficult to drill. If they are annealed at 750°C. for a couple of hours, they will become soft enough to drill.

Process of Analysis.—Place 2 grams of the drillings in a 200-c.c. casserole and add 40 c.c. of hydrochloric acid (sp. gr. 1.19) and heat nearly to boiling. When action ceases, add from time to time a few drops of nitric acid until the steel is entirely decomposed. In this way the sample is dissolved without the separation of WO_3. When decomposition is complete add 5 c.c. HNO_3, evaporate to dryness, dissolve the residue with 60 c.c. of 1:1 HCl, heating until all iron is dissolved, add 50 c.c. of water and heat for a few minutes longer, then filter through an 11-cm. filter paper. Again evaporate to dryness, dissolve and filter. Wash thoroughly with 1:10 HCl until the precipitate is free from iron. Chromium and vanadium may be determined in the filtrate.

The filter contains the tungsten as WO_3 and the SiO_2 more or less contaminated with chromium and iron oxides. Dry the filter and contents, ignite in a platinum crucible until all carbon is removed, cool and weigh. Add several cubic centimeters of HF, evaporate to dryness, ignite carefully and again weigh. The loss in weight is the SiO_2.

The filtrate contains a small amount of tungsten which can be recovered with cinchonine. (See page 140.)

Add to the impure WO_3 in the crucible 5 grams of sodium carbonate and a few milligrams of tartaric acid and fuse the mixture until all the tungsten is dissolved. Cool, digest the cake with 100 c.c. of water until no hard lumps remain and the sodium tungstate is completely dissolved. Filter through a small filter paper and wash with hot water until the washings are non-alkaline when tested with phenolphthalein. Burn off the filter paper, ignite and weigh the residue of Fe_2O_3 and Cr_2O_3. Subtract the weight of this residue from the last weight of the impure WO_3; the difference is WO_3, which, multiplied by 0.7931, gives the weight of tungsten in the sample.

Analysis of Ferrotungsten.—Ferrotungsten is not soluble in acids without the use of HF, hence this alloy must be fused with 10 times its weight of sodium peroxide in a nickel crucible if it is desired to determine the silicon in the tungsten. If the tungsten only is desired, the ground sample is dissolved with 5 c.c. of HF in a platinum dish. When action is over, add HNO_3, a few drops at a time, until decomposition is complete, add 10 c.c. 1:1 H_2SO_4 and proceed as above directed, using cinchonine to recover the tungsten in the filtrate as directed in the notes below.

Notes on the Tungsten and Silicon Determinations.—When the steel is dissolved in strong hydrochloric acid as above directed, the tungstic acid does not form until the iron is dissolved and the precipitate is not much contaminated with iron. Since a trace of tungstic acid remains in solution after the first evaporation, also some silica, it is necessary to evaporate the filtrate to dryness again to render both insoluble by dehydrating the tungstic acid and silicic acid forming the insoluble anhydrides, WO_3 and SiO_2. But a fairly accurate determination of tungsten may be made by omitting the second evaporation to dryness.

Tungstic anhydride is volatile if ignited at a much higher temperature than a dull red, hence the necessity for heating carefully.

There will always be a little WO_3 which adheres to the casserole and cannot be removed by a policeman. It can be removed as follows: When the casserole is well washed out and the filter paper and precipitate thoroughly washed, wet a piece of filter paper with NH_4OH and wipe out the casserole with it. This will remove all the tungstic acid adhering to the casserole. Add the paper to the other two papers and ignite them all together.

If the chromium in the filtrate is not desired and a tungsten determination alone is wanted, it is not necessary to evaporate the the filtrate from the WO_3 to dryness. Proceed as follows: Add to the filtrate 20 c.c. of 1:1 hydrochloric acid solution containing 0.5 gram of cinchonine. The cinchonine precipitates the tungsten completely. Heat the solution and filter and wash with a dilute acid solution of cinchonine. Ignite the precipitate with the rest of the precipitate of WO_3.

When the filtrate from the WO_3 is evaporated to fumes of sulfuric acid, the HCl is expelled. This is necessary before the chromium is determined. The sulfates will dissolve slowly, but it is not necessary to wait until they are all dissolved before adding the permanganate to oxidize the chromium to chromic acid. The reactions involved in the chromium determination are given under the determination of vanadium and chromium.

If the presence of molybdenum is suspected, the filtrate from the fusion of the WO_3 should be tested for molybdenum as directed on page 144. If molybdenum is found it should be determined.

When a sulfuric acid evaporation is used a small amount of tungsten goes into solution, the amount dissolving increasing with the amount of phosphorus in the alloy, and cinchonine must be used to precipitate this small amount. Add 10 c.c. of HCl containing 0.5 gm. of cinchonine, heat and filter immediately. Wash with dilute cinchonine solution 10 times, ignite very slowly and weigh the WO_3. This weight is added to the weight of the main portion of the WO_3.

Cinchonine Solution.—Dissolve 125 grams of cinchonine in 1,000 c.c. of 1:1 HCl.

Volumetric Method for Tungsten.—Wash the precipitate of WO_3 obtained as above directed with a hot dilute hydrochloric acid solution until the iron salts are gone, then wash with a 5 per cent solution of KNO_3 until the washings are free from acid. It is not necessary that the WO_3 be all removed from the casserole as directed for the gravimetric method. Put the filter and contents in the casserole, run in from a burette about 60 c.c. of a N/10 sodium hydroxide solution and stir the paper about until all the WO_3 is dissolved. Then add a few drops of phenolphthalein and titrate the excess of soda with N/10 HCl until the pink color disappears. The number of cubic centimeters of soda used minus the number of cubic centimeters of acid used multiplied by 0.0092 divided by the weight of the sample used and multiplied by 100 gives the percentage of tungsten.

The titration reaction is $WO_3 + 2NaOH = Na_2WO_4 + H_2O$. If the WO_3 is very impure with iron the end point of the titration is unsatisfactory. (See LINDE and TRUEBLOOD, *J. Am. Chem. Soc.*, **29**, 477.)

CHAPTER XIII

DETERMINATION OF MOLYBDENUM IN STEELS, FERRO-ALLOYS AND ORES

Molybdenum is found in ores chiefly as the minerals molybdenite (MoS_2) and wulfenite ($PbMoO_4$). Metallic molybdenum, as ferro-molybdenum, is added to steel to produce one of the many varieties of high-speed steel in conjunction with tungsten, chromium, vanadium and, occasionally, cobalt. It is also added in small percentages to special steels where especial resistance to wear is demanded, such as in gears.

The determination of molybdenum is satisfactorily accomplished by both gravimetric and volumetric methods. The volumetric method, most widely used, depends upon the same reactions as those used in the Emmerton process for the determination of phosphorus, as given on page 56, whereby the molybdenum is reduced from hexavalent to trivalent condition and then reoxidized by standard permanganate.

Molybdenum is determined gravimetrically by precipitating as sulfide and converting the sulfide to oxide, which is weighed, or by precipitating as lead molybdate, which is weighed as such.

Molybdenum can be separated from most interfering elements by precipitation with H_2S in a slightly acid solution, or by fusion with sodium peroxide, forming sodium molybdate, which can be extracted from iron, titanium, etc. with water.

Process of Analysis of Steels.—Dissolve 2 grams of the sample in 100 c.c. of water and 50 c.c. of 1:1 H_2SO_4, heating until everything is dissolved. When solution is practically complete add 1 gram of ammonium persulfate and boil until the persulfate is decomposed. Cool and nearly neutralize with ammonia, heat to boiling and pass hydrogen sulfide through the solution at a rapid rate for 15 minutes. Keep the solution hot for several hours while a slow stream of H_2S is passing. Filter off the sulfides of molybdenum, arsenic and copper and wash with a 2 per cent H_2SO_4 solution saturated with H_2S. The filtrate will contain traces of molybdenum and should be allowed to stand in a pressure bottle for several hours after saturating with H_2S.

Gravimetric Method.—Wash the precipitate of sulfides into a 400-c.c. beaker, set the beaker under the funnel and dissolve the sulfides remaining on the filter by washing with 20 c.c. of hot 1:1 HCl, alternating with bromine water. Dilute the filtrate to 100 c.c., add 20 c.c. of HCl and 3 grams of sodium chlorate and boil until the molybdenum sulfide is completely dissolved. Filter and wash well.

To the filtrate add 20 per cent NaOH solution until decidedly alkaline, boil, allow the precipitate to settle and filter off ferric hydroxide, etc. If the precipitate is large, dissolve in hot HCl and reprecipitate, adding the filtrate to the main filtrate. To the filtrate, having a volume of about 200 c.c., add 1:4 HCl until 5 c.c. excess is used, add 50 c.c. of 50 per cent ammonium acetate solution, heat to boiling and slowly add lead acetate solution prepared as directed. Use ½ c.c. of lead acetate solution for each milligram of molybdenum present and an excess of 5 c.c. This can be best accomplished by adding the lead acetate slowly and with stirring until further addition produces no increased cloudiness, then add 5 c.c. excess, boil the solution for 10 minutes, and allow the precipitate to settle until the solution is clear. Filter and wash 15 times with hot water, transfer the paper and precipitate to a porcelain crucible and ignite very slowly at first and, finally, when the carbon is all gone (use a red-heat), cool and weigh. The weight of the lead molybdate multiplied by 0.2614 gives the molybdenum.

Lead Acetate Solution.—Add 10 c.c. of glacial acetic acid to 990 c.c. of water and dissolve in the solution 10 grams of lead actetate.

Volumetric Method.—Wash the molybdenum sulfide as obtained above into a 250-c.c. beaker with 50 c.c. of 1:1 HNO_3 containing free bromine. Ignite the paper (with a trace of residue) transfer the ash to the beaker, add 5 grams of sodium chlorate and 25 c.c. of 1:1 H_2SO_4 and boil until copious fumes of SO_3 are evolved. Cool, add 5 c.c. of HNO_3 and again evaporate until the SO_3 is copiously evolved (it is essential that the nitric acid should be completely expelled). Cool, add 100 c.c. of water and heat nearly to boiling, which should give a clear solution. Add 2 grams of pure granulated zinc and boil until the zinc is nearly dissolved. This treatment partially reduces the molybdenum and precipitates all the copper and eliminates the arsenic. Filter through asbestos. Prepare the Jones reductor as shown on page 39, except that the tip of the reductor should be lengthened so as to reach to the bottom of the flask, put in 2 c.c. of the ferric sulfate-phosphate solution for each 0.01 gram of molybdenum supposed to be present and sufficient water to cover the end of the reductor tube.

The reductor should be filled with 2 per cent H_2SO_4 before it is used to reduce the molybdenum.

Again add 2 grams of zinc to the sulfuric acid solution of the molybdenum, heat for five minutes, then pour the solution into the reductor, using sufficient suction to allow 20 c.c. to pass through the reductor per minute. When all the molybdenum solution has been poured into the reductor, wash the beaker with hot water and, finally, pass through the reductor 200 c.c. of warm 2 per cent H_2SO_4. At no time must the reductor be allowed to become empty so that air can suck into the flask.

The reduced molybdenum ($(Mo_2(SO_4)_3)$) is a clear green in color, but as soon as it comes into contact with the ferric solution it changes to red, owing to oxidation by ferric iron with corresponding reduction of the iron. Titrate immediately with a standard permanganate solution until a faint pink is obtained.

If a decinormal solution is used, each cubic centimeter will titrate 0.0032 gram of molybdenum; if the iron value of the permanganate is known, each cubic centimeter will titrate molybdenum equal to the iron value multiplied by 0.5748.

Ferric Sulfate-phosphate Solution.—Dissolve 100 grams ferric sulfate, 150 c.c. phosphoric acid (1.75 sp. gr.) and 20 c.c. sulfuric acid (1 : 1) in 830 c.c. water.

Notes on the Process.—The residue left after molybdenum sulfide is dissolved may contain some molybdenum. Test it as follows: Digest the paper and residue with 20 c.c. HNO_3, 10 c.c. H_2SO_4, and 5 grams of sodium chlorate. Heat until the solution is clear, boil to dense fumes of SO_3, and cool. Add 20 c.c. of 1 : 5 HCl and 10 c.c. of 1 : 1 H_2SO_4, 5 c.c. of 5 per cent KCNS and 10 c.c. of 25 per cent $SnCl_2$ solution. If molybdenum is present, the solution will become red, the depth of red color depending upon the amount of molybdenum present. The amount of molybdenum can be determined by comparison against standard solution, and correction made.

The zinc used in the volumetric process always contains some iron which titrates as molybdenum. Hence a blank determination must always be made. The permanganate should be standardized against iron as directed on page 37, and also against a sample containing a known amount of molybdenum. The volumetric method depends upon reducing the molybdenum by zinc under carefully controlled conditions. The analyst should run several tests to find just how rapidly the solution may be run through the reductor and complete reduction be attained. The amalgamated zinc should be of 20-mesh size, amalgamated with ½ gram of mercury to 150 grams of zinc and should contain less than 0.01 per cent iron. After having been used for forty or fifty determinations, the zinc should be renewed. The reduced molybdenum is oxidized by contact with air, hence no air should be drawn through the reductor and the reduced solution must be titrated immediately.

When blanks are properly made and care is used in the volumetric determination, results should be accurate to 0.03 per cent.

The use of the ferric phosphate solution in the reductor flask makes the end point sharper and reduces the danger of oxidation of the solution upon exposure to the air, since the ferric iron oxidizes molybdenum, producing ferrous iron which is less easily oxidized by air. The titration by permanganate really consists, then, in titrating divalent iron which has been quantitatively produced by reduction with trivalent molybdenum. The reactions are: $3Fe_2(SO_4)_3 + Mo_2(SO_4)_3 + 8H_2O = 6FeSO_4 + 2H_2MoO_4 + 6H_2SO_4$. The reduced iron is oxidized by permanganate by the well-known reaction.

The gravimetric determination of molybdenum as lead molybdate is a very accurate and reliable method. It is not interfered with by large amounts of salts. The molybdate can be precipitated in faintly acid solutions free from impurities in the presence of copper, cobalt, nickel, zinc, manganese, magnesium and mercury, barium, strontium, uranium, arsenic, cadmium and aluminium. Cobalt, vanadium and tungsten interfere but are separated from the molybdenum by hydrogen sulfide.

Process for Ferromolybdenum.—Dissolve ½ gram of the finely crushed sample with 10 c.c. of 1:3 HNO_3, 10 c.c. of 1:1 H_2SO_4 and a few drops of HF. When solution is complete, evaporate to fumes of SO_3. Cool, add 50 c.c. of water, heat until solution is complete, cool and nearly neutralize with ammonia, but not until the solution takes on a red tint. Heat nearly to boiling and pour very slowly and with vigorous stirring into 75 c.c. of hot ammonium hydroxide. Wash the beaker in which the solution was made with dilute ammonia, transferring the washings to the main solution. Add paper pulp obtained by macerating two 9-cm. papers, stir well and filter on an 11-cm. filter paper. Wash thoroughly with hot water, wash the precipitate back into the beaker, dissolve in a slight excess of H_2SO_4, nearly neutralize with ammonia and again pour slowly and carefully into 75 c.c. of 15 per cent ammonia nearly boiling. Filter and wash as before, combine the two filtrates in a 500-c.c. beaker, add 3 grams of tartaric acid and pass a rapid stream of H_2S through the warm solution. The solution becomes a deep red, owing to the formation of thiomolybdate. The small amount of sulfides which form is filtered and washed thoroughly with H_2S water.

Warm the solution and add 1:1 H_2SO_4 until the solution becomes slightly acid. This point is marked by the cessation of effervescence and the disappearance of the red color. Allow the molybdenum sulfide to settle, filter and wash with hydrogen sulfide water until all salts are removed. The water should be slightly acid with H_2SO_4.

The filtrate from the MoS_3 contains some molybdenum. Add 15 c.c. of HNO_3 and 5 c.c. of H_2SO_4, evaporate until dense fumes of SO_3 are obtained, cool, add 10 c.c. more HNO_3 and again evaporate to fumes and the removal of most of the H_2SO_4. This destroys all organic matter. Cool, dissolve in 50 c.c. of water, add 2 grams of tartaric acid and ammonia until alkaline and 10 c.c. in excess, warm and saturate it with H_2S. Filter any precipitate which is formed, acidify the filtrate with 1:1 H_2SO_4 and filter the molybdenum sulfide as above.

Finish the analysis by either volumetric or gravimetric method as described above, except that more sodium chlorate will be needed to oxidize the molybdenum sulfide.

Process for Ores.—Proceed exactly as directed for ferromolybdenum. If vanadium and tungsten are absent, the process may be greatly shortened by omitting the hydrogen sulfide precipitation, but it is always safest to assume that they are present.

Note.—The tartaric acid is used to prevent vanadium and tungsten from precipitating as sulfide with the molybdenum.

REFERENCES:

BONARDI and BARRETT, *Tech. Paper* 230, U. S. Bureau of Mines.
PETTY, *The Chemist-Analyst*, no. 30 (1920).
CAMP and MARDEN, *J. Ind. Eng. Chem.*, **12**, 998.
U. S. Steel Corporation, "Methods for the Analysis of Alloy Steels."
RANDALL, *Am. J. Sci.*, **24** (1907), 313.

CHAPTER XIV

THE DETERMINATION OF TITANIUM

Titanium may be present in steels up to a few tenths per cent. It is generally present in pig iron in small amounts. In ferrotitanium there may be as high as 75 per cent present. Ores contain from nearly zero up to a good many per cent of titanium.

In steels the titanium is present as solid solution in iron and as crystals of titanium nitride and titanium cyanamide. The titanium present in solid solution is soluble in acids, the rest is insoluble. Ores contain titanium chiefly as the minerals rutile (TiO_2), ilmenite ($FeTiO_3$), titanite ($CaTiSiO_5$) and other less important minerals.

Titanium may be determined gravimetrically by weighing as TiO_2, or volumetrically by reduction with zinc to trivalent condition followed by titration with permanganate. When present in amounts below 0.5 per cent, it is best determined colorimetrically. This is done by adding hydrogen peroxide to the 5 per cent sulfuric acid solution and producing a yellow color which is compared with a standard solution treated in the same way. The peroxide oxidizes the titanium to the hexavalent form.

Titanium may be separated from iron when the iron is divalent by boiling the dilute, slightly acid solution, when the titanium precipitates out as titanic acid. Or the titanium may be separated from the iron when to the acid solution containing the iron in the ferrous condition is added an excess of ammonia containing enough alkali cyanide to form ferrocyanide with the iron. The ferrocyanide stays in solution, while the titanium precipitates as $Ti(OH)_4$. This precipitate, whether made from acid or alkaline solution, if formed from a solution containing large amount of iron, is always impure. If the precipitate is then fused with sodium carbonate and the fusion is extracted with water, the titanium remains insoluble as sodium titanate, while phosphorus, silica, chromium, aluminium and vanadium go into solution. The titanate is dissolved in acid, the $Ti(OH)_4$ is again precipitated and weighed as TiO_2.

Titanium is more easily precipitated from an acid solution when phenylhydrazine ($C_6H_5.NH.NH_2$) is used.

$Ti(OH)_4$ cannot be precipitated from solutions containing tartaric acid, from which solutions iron may be precipitated as sulfide.

The presence of zirconium hinders the precipitation of titanium by hydrolysis from an acid solution. It can be separated from zirconium by precipitating zirconium in weakly acid solution, as phosphate in the presence of H_2O_2, which prevents the titanium from precipitating. Titanium may be precipitated from tartrate solutions from which iron has been removed as sulfide by the use of "Cupferron" (ammonium nitrosophenylhydroxylamine) in a dilute acid solution.

Process of Analysis (Colorimetric).—Add to 1 gram of the drillings in a 500-c.c. flask 40 c.c. of 1:3 sulfuric acid. Heat to boiling until no more action takes place. Pay no attention to any residue. Dilute to 250 c.c. and add NH_4OH until a slight precipitate forms, then add a few grams of sodium thiosulfate and a few drops of sulfuric acid, or enough to make the solution clear. Heat until all the iron is reduced, as shown by a test of a drop with KCNS, then add a solution containing 25 c.c. of water, 15 c.c. of NH_4OH (sp. gr. 0.9) and 10 grams of KCN. Heat to boiling for several minutes. Prepare a filter by shaking two 9-cm. filter papers in a flask until well macerated and then pouring the pulp through a funnel containing a platinum cone. Place this funnel in a suction flask and pour the solution through, using suction. The solution should filter quickly to prevent oxidation of the iron. Wash well with water.

Burn the paper and its contents in a platinum crucible until all the paper is consumed, then add 4 grams of $KHSO_4$ which has been previously fused to remove the water and fuse and maintain at a bright red-heat for several minutes. Cool, then add water enough to half fill the crucible and 5 c.c. of sulfuric acid, and heat until the cake is all dissolved. Cool, transfer to a Nessler tube or other color comparitor, dilute to 100 c.c. and add 3 c.c. of hydrogen peroxide (ordinary 3 per cent solution). If titanium is present a yellow color will immediately appear. To the other tube add 100 c.c. of 5 per cent sulfuric acid, 3 c.c. of peroxide and standard titanium sulfate solution a little at a time, shaking after each addition, until the color matches the color in the solution of titanium from the sample. The titanium in the sample will then be the same as that added for comparison.

The above method is very accurate, only requires about 1½ hours and vanadium does not interfere, as it would if the sample were compared directly. A Government standard sample containing 0.073 per cent. Ti gave 0.075 per cent by the above method, even when 3 per cent of vanadium was added.

Gravimetric Method.—Fuse the precipitate obtained above with 20 times its weight of sodium carbonate and a little KNO_3 until in quiet fusion, dissolve in hot water and wash with sodium carbonate solution (5 per cent). Wash at least 10 times. Place the paper and residue of sodium titanate in a platinum crucible and fuse with $KHSO_4$ at a bright red until in clear fusion. Cool, dissolve in hot water containing sulfuric acid, add NH_4OH until nearly but not quite alkaline, then a gram or so of thiosulfate to reduce what little iron may be present and, finally, add a solution of 25 c.c. of water, 15 c.c. of NH_4OH and 1 gram of KCN. Heat to boiling and filter through a pulp filter as above directed. Wash well to remove alkali salts and, if the amount of titanium is not high, ignite and weigh the TiO_2. It should be ignited over the blast. If the sample is very high in titanium, as in a ferrotitanium, the precipitate will carry down some alkali salts and should be dissolved in sulfuric acid 1:3 and precipitated again with NH_4OH. The weight of the precipitate multiplied by 0.6005 gives the titanium.

Ores are analyzed as follows: Place 1 gram of the finely ground sample in a platinum crucible, add 10 grams of sodium carbonate and fuse until the fusion is quiet. Cool, dissolve in hot water and wash well to remove as much silica and alumina as is possible. Ignite the paper and residue in a platinum crucible, fuse with $KHSO_4$, dissolve in hot water containing 5 c.c. of sulfuric acid and proceed as with the first solution of the metal in sulfuric acid as given above, for either the colorimetric or gravimetric method.

Notes on the Process.—When a metal is dissolved in sulfuric acid it will go into solution mostly as ferrous iron, so that not much thiosulfate will be required. When the sample is an ore, more care will be required to get all the iron reduced.

The precipitate of $Ti(OH)_4$ from an alkaline solution has no tendency to run through the filter. If the filter is a pulp one, the filtration will be rapid, but if a filter paper is used, it will be slow.

$Ti(OH)_4$ has a strong tendency to stick to the glass, so that the precipitations should all be made in the same flask. Finally, it is well to heat the flask with 5 c.c. of strong sulfuric acid until it fumes strongly and then determine the titanium thus obtained colorimetrically.

There must be no fluorine in the solution to be analyzed colorimetrically as it discharges the color of titanium with hydrogen peroxide. Also, large amounts of alkali sulfates effect a slight weakening of the color.

Both chromium and aluminium precipitate from alkaline solution with titanium and should be removed upon solution of the sodium carbonate fusion when the gravimetric method is used. They do no harm in the colorimetric method. The KNO_3 is used to oxidize the chromium to chromate.

It must not be forgotten that KCN is very *poisonous* and the solution containing it must not be made acid except with the greatest care and in a good hood.

The precipitate of $Ti(OH)_4$ may contain a little nitride after ignition and be brown. If it is, it should be fused with sodium carbonate again and reprecipitated from a solution only slighly alkaline with NH_4OH.

REFERENCE:

BORNEMAN and SCHIREMEISTER, *Metallurgie*, **7**, 71, 723.

Precipitation from Acid Solution.—Dissolve 5 grams of the drillings with 100 c.c. of 1:1 HCl, heating until action ceases, dilute to 200 c.c., add 3 grams of sodium chlorate and boil until any tungsten, if present, is converted to yellow WO_3. Filter the WO_3 and wash with 10 per cent HCl until all iron color is removed.

Dissolve the WO_3 by washing from the filter paper into a small beaker and adding 5 c.c. of ammonia. Filter (rejecting the filtrate) and wash the residue on the paper 10 times with dilute ammonia. Burn the paper, dissolve the residue in a few drops of HCl and add to the main solution. Dilute the solution to 300 c.c., add ammonia until slightly alkaline, then HCl until barely acid, then 3 c.c. more. Add 25 grams of sodium thiosulfate dissolved in 50 c.c. of water, then boil the solution for 10 minutes. The thiosulfate reduces the iron to divalent form. Add 3 c.c. of phenylhydrazine and continue the boiling several minutes. The titanium usually precipitates without the use of the phenylhydrazine, which merely makes the precipitation more certain.

Add paper pulp obtained by macerating a small filter and filter and wash the precipitate with hot water five times. Burn the paper in a platinum crucible and fuse the residue containing

TiO_2 (with varying amounts of Fe_2O_3, Al_2O_3, etc.) with 3 grams of sodium carbonate and a few particles of sodium nitrate until the fusion is clear. Cool and disintegrate the fusion with hot water until no hard particles remain, filter and wash thoroughly with hot water. Chromium, alumium, vanadium and phosphorus pass into the filtrate, leaving the titanium with a small amount of iron oxide on the paper.

Dissolve the residue on the filter paper with 10 c.c. of hot 1:1 HCl, and wash until the filtrate does not taste acid. Add ammonia until the solution is slightly alkaline, then add HCl until slightly acid and add 1 gram of sodium thiosulfate. Heat until the solution gives no test for ferric iron when a drop is tested on a white plate with KCNS solution. Add 5 c.c. of NH_4OH and 1 gram of KCN and boil for a minute. Add a small amount of macerated filter paper pulp and filter through a small paper. Wash well with water slightly ammoniacal. Burn the paper and its contents in a platinum crucible until all carbon is gone and weigh the TiO_2.

Colorimetric Method.—Dissolve the impure residue of sodium titanate obtained above by placing the paper and contents in a beaker containing 50 c.c. of warm 1:4 H_2SO_4 and heating until all titanium is dissolved. Filter, wash with dilute sulfuric acid and determine colorimetrically as directed on page 149.

Notes.—If the steel or alloy is free from tungsten the sample can be dissolved in 1:1 HCl as above directed, but without the use of chlorate, and the process greatly shortened by adding only 2 grams of thiosulfate because the iron is already in the divalent condition.

Standard Titanium Sulfate Solution.—Dissolve 0.52 gram of ignited TiO_2 as follows: Fuse the TiO_2 with 6 grams of sodium carbonate, cool and disintegrate the fusion in 50 c.c. of water, add 100 c.c. of 1:4 H_2SO_4 and heat until the solution is perfectly clear, dilute exactly to 500 c.c., pipette 20 c.c. of this solution into a beaker, and determine the amount of titanium by the gravimetric method as described above.

Peroxide Solution.—To 750 c.c. of water add 250 c.c. of 1:1 H_2SO_4, then add 7 grams of sodium peroxide, a small amount at a time, shaking the solution after each addition.

REFERENCES:

HILLEBRAND, *Bull.* 700, U. S. Geol. Survey, p. 128.
BASKERVILLE, *J. Soc. Chem. Ind.* (1910), 419.
ETTELE, *Chemist-Analyst*, no. 27.
BROWN, *J. Amer. Chem. Soc.*, **39**, 2358 (use of Cupferron).

Process for Ferrotitanium.—Dissolve 1 gram of sample with 50 c.c. of 1:4 H_2SO_4 and, when effervescence ceases, evaporate until fumes of SO_3 appear. Cool, add 100 c.c. of water and heat to dissolve iron salts, filter and wash with dilute H_2SO_4 10 times, ignite until all the carbon is burned off, then more intensely for 10 minutes, cool and weigh. Add a few drops of sulfuric acid and several cubic centimeters of HF, evaporate to dryness, ignite, cool and weigh. The loss in weight is SiO_2. Add any residue in the crucible to the filtrate from the silica. Dilute to 400 c.c., add ammonia until a faint precipitate is obtained, then 1 c.c. of HCl, 10 c.c. of glacial acetic acid and 10 grams of sodium thiosulfate dissolved in 50 c.c. of water. Heat to boiling and continue the boiling for 10 minutes and allow to settle. Filter and wash a half dozen times with dilute acetic acid (2 per cent), ignite the paper and precipitate in a platinum crucible until carbon is all gone, add 5 grams of sodium carbonate and fuse until the fusion is quiet. Cool, add 50 c.c. of water and heat until the fusion is disintegrated and no hard particles remain. Filter through a small filter paper and wash well with hot water, put the paper and impure sodium titanate in a beaker, add 25 c.c. of 1:2 HCl and heat until the titanate is all dissolved, filter again through a small filter, wash well with hot water, neutralize with ammonium hydroxide and precipitate again as above directed. Wash the precipitate with 2 per cent acetic acid 15 times, or until no test for chloride is obtained with silver nitrate. Ignite slowly at first to burn off the paper and finally intensely, cool and weigh the TiO_2. This weight multiplied by 0.6005 gives the titanium.

Process for Ores.—Fuse 1 gram of the ore with 8 grams of Na_2O_2 in an iron crucible, cool, disintegrate with water, filter and wash 10 times with hot water. Handle the sodium titanate exactly as if it were a sample of ferrotitanium.

REFERENCE:

WADDELL, *Analyst*, **44** (1919), 307–309.

CHAPTER XV

THE DETERMINATION OF COPPER IN IRON AND STEEL

When iron is dissolved in dilute sulfuric or hydrochloric acid in the absence of oxygen the copper remains behind undissolved. Any traces of copper that dissolve are removed from solution by hydrogen sulfide.

Colorimetric Method.—Dissolve 10 grams of drillings in a mixture of 25 c.c. (1.84 sp. gr.) sulfuric acid and 250 c.c. of distilled water, using a 500-c.c. flask. Heat carefully until the borings have dissolved, dilute to 400 c.c. with distilled water and add 0.5 gram of zinc sulfide, cork the flask for a few minutes, filter on an 11-cm. paper, wash the residue with hydrogen sulfide water, open the paper against the side of the funnel, add 20 c.c. of hot nitric acid (1.18 sp. gr.) to the residue on the paper, allowing the solution to run into the flask in which the borings had been dissolved.

Wash the paper with 2 per cent nitric acid solution, evaporate the filtrate to about 15 c.c., remove from the hot plate and add ammonia water (1:3) just sufficient to precipitate the ferric hydroxide.

Filter into a 100-c.c. Nessler tube and wash with hot water, cool to tap-water temperature. The presence of copper will be indicated by the blue color of the filtrate from the ferric hydroxide. To another Nessler tube add about 50 c.c. of distilled water and 5 c.c. of (1:3) ammonia water. Then add from a burette a standard copper solution until the colors match when diluted to the same volume.

Modification.—It is sometimes found convenient to modify this method for determining copper. After determining the sulfur by the evolution method, the hydrochloric acid solution can be used for the determination of this element as follows:

The solution from the determination of sulfur is neutralized with ammonia until there is a slight precipitate of ferrous hydroxide. Acidify with 5 c.c. of hydrochloric acid, heat to boiling point, add 0.5 gram of zinc sulfide, when dissolved dilute to 400 c.c. with distilled water and cork the flask for a few minutes. When the Cu_2S has settled, filter rapidly on an 11-cm. paper. Wash with hydrogen sulfide water and finish the determination as previously described.

Notes.—The success of the colorimetric method for determining copper depends upon carefully following each detail. Sometimes a green color will be obtained instead of a blue. This is usually due to the use of too much ammonia and can be corrected by acidifying the green solution with dilute sulfuric acid (1:1) and then making the solution faintly ammoniacal.

Make the standard solution by dissolving 3.928 grams of $CuSO_4$, $5H_2O$ in water and diluting to 1 liter. One cubic centimeter contains 0.001 gram of copper.

Instead of determining the copper colorimetrically, it may be determined in the final nitric acid solution electrolytically or by the iodine method, or very satisfactorily by precipitating as CuCNS and weighing as directed below.

Sulfo-cyanate Method.—Proceed as above directed until the ammonia solution of copper is obtained. Precipitate the copper as directed on page 242 as CuCNS, filter the CuCNS on an asbestos mat in a Gooch crucible which has been accurately weighed. Wash thoroughly, dry at 105°C. and weigh. The weight of the CuCNS multiplied by 0.523 gives the copper. This method is very accurate and is recommended as the best.

Iodide Method.—The colorimetric method for determining copper is not sufficiently accurate when this element is in excess of 0.15 per cent. When such is the case, proceed as outlined for the determination of this element by the colorimetric method to the point where dilute ammonia is added to precipitate the ferric hydroxide. Instead of filtering into a 100-c.c. Nessler tube, use a 250-c.c. beaker for this purpose.

After washing a few times with hot water, dissolve the ferric hydroxide with hot dilute hydrochloric acid, allowing the solution to run into the flask in which the original precipitation was made, wash a few times with hot water, add ammonia water (1:3) just sufficient to precipitate the ferric hydroxide and leave a very slight excess of ammonia present, heat to boiling, filter, and allow the filtrate to flow into the 250-c.c. beaker containing the major portion of the copper.

Add 5 c.c. of sulfuric acid (1.84 sp. gr.) evaporate on a hot plate to dense fumes, cool, add 20 c.c. of water, make slightly alkaline with ammonia, boil off the excess ammonia, then neutralize with glacial acetic acid, adding 5 c.c. in excess, cool and add 5 grams of potassium iodide crystals, then a few cubic centimeters of starch solution and titrate with N/20 sodium thiosulfate solution to the disappearance of the blue color.

The thiosulfate can be conveniently standardized by using 25 c.c. of the standard copper sulfate solution described in the "Colorimetric Method" for determining copper, adding the same reagents and titrating under the same conditions as described in the regular method.

If preferred, the thiosulfate can be standardized by dissolving 5 grams of potassium iodide in 500 c.c. of water, adding 25 c.c. of concentrated hydrochloric acid, then exactly 25 c.c. of standardized N/10 potassium bichromate solution. Add starch solution and titrate with the thiosulfate solution to the disappearance of the blue color. Each cubic centimer of N/10 potassium bichromate solution equals 0.00636 gram copper.

Standard Starch Solution.—The starch solution used in this method is prepared as described under the determination of sulfur in iron and steel, page 97.

Copper in Steels Containing Tungsten.—Dissolve the sample as directed under the determination of tungsten in tungsten steels, finally evaporating to fumes of sulfuric acid. Add 10 c.c. more of 1:1 H_2SO_4, heat, cool, add 50 c.c. of water and heat until all salts are dissolved. Filter and dilute to 300 c.c., add 50 c.c. of 50 per cent sodium thiosulfate solution, heat to boiling for five minutes, filter off the copper sulfide and proceed as usual.

REFERENCE:

"Methods of Analysis of Iron and Steel at American Rolling Mills Company."

CHAPTER XVI

DETERMINATION OF ARSENIC IN IRON AND STEEL

This element may be estimated by dissolving 10 grams of the metal in HNO_3 (sp. gr. 1.2) evaporating and baking as for phosphorus, dissolving the residue in concentrated HCl without heating, which might volatilize $AsCl_3$, diluting, reducing with Na_2SO_3 and precipitating with H_2S as As_2S_3. The As_2S_3 is then oxidized by fuming HNO_3, precipitated with magnesia mixture and weighed as $Mg_2As_2O_7$. For details, see Fresenius' "Quantitative Analysis." The arsenic may be satisfactorily titrated by iodine.

The following method is much shorter and is sufficiently accurate when only small percentages are present. It depends upon the volatilization of As as $AsCl_3$ when a solution containing it is boiled with HCl and a large excess of ferric and ferrous chloride. In order that the volatilization may be rapid and complete, the liquid should have its boiling point raised to about 108°C. by the addition of $ZnCl_2$ or $CaCl_2$ and should contain concentrated HCl.

Process of Analysis.—Dissolve 20 grams of drillings in a 6-in. diameter casserole, using 300 c.c. of nitric acid (1.20 sp. gr.). Heat slowly in order to prevent the reaction from becoming too violent. Evaporate to dryness on a hot plate and bake until no more nitrous fumes are evolved. Remove from the hot plate and allow to cool, transfer the ferric oxide to a distillation flask to which is attached a 50-c.c. pipette which dips into a beaker containing 200 c.c. of distilled water. Place in the distillation flask 40 grams of cuprous chloride and 300 c.c. of concentrated hydrochloric acid, boil until about two-thirds of the hydrochloric acid has distilled over.

From the beginning of the distillation pass hydrogen sulfide gas into the distillate while it is being heated almost to the boiling point. This will insure a rapid precipitation of arsenious sulfide, which settles readily and can be easily filtered. After the distillation is discontinued remove the beaker containing the distillate from the source of heat, dilute to 500 c.c. with cold water and continue to pass hydrogen sulfide gas into the solution until cold. Disconnect the pipette and rinse inside and outside with 2 or 3 c.c. of concentrated ammonia, allowing the washings to run into the beaker containing arsenious sulfide.

Allow the precipitate to settle and filter on asbestos, using a Gooch crucible, wash with distilled water until free from acid. Transfer the asbestos felt containing the arsenious sulfide to a 250-c.c. beaker. Add 10 c.c. of fuming nitric acid or 10 c.c. of nitric acid (1.42 sp. gr.) and 1 gram of potassium chlorate. Evaporate to dryness. Dissolve the arsenic acid in dilute hydrochloric acid, filter and wash with hot distilled water. Concentrate to about 20 c.c., heat to boiling and add 10 c.c. of magnesia mixture, and 10 c.c. of ammonia (0.95 sp. gr.). Continue to boil for 15 minutes, remove from the source of heat, cool, add 20 c.c. of alcohol and let stand for five hours. Filter and wash the precipitate on a weighed Gooch crucible, dry, ignite and weigh as magnesium pyroarsenate, which contains 48.27 per cent arsenic.

Magnesia Mixture.—Dissolve 110 grams of crystallized magnesium chloride in a small amount of water. Add 140 grams of ammonium chloride, make distinctly ammoniacal with ammonia and dilute to 2,000 c.c. with distilled water. Allow the solution to stand and siphon off the clear solution for use.

REFERENCES:

GIBB, *J. Soc. Chem. Ind.* (1901), 184.
NORRIS, *J. Soc. Chem. Ind.* (1902), 393.
BLAIR, "The Chemical Analysis of Iron," p. 201.
STEAD, *J. Iron Steel Inst.*, **1** (1895).
"Methods of Analysis of Iron and Steel at American Rolling Mills Company."

Instead of weighing the arsenic as pyroarsenate the iodine titration method is often used. For this method proceed as directed on page 223, using the arsenic sulfide obtained above.

CHAPTER XVII

DETERMINATION OF ALUMINIUM IN IRON AND STEEL

Metallic aluminium is added to steel in nearly all steel works to deoxidize or "quiet" the steel. The affinity of aluminium for oxygen is so much greater than that of iron that very small amounts of aluminium are sufficient to overcome the mass action of the large amount of iron present forming Al_2O_3, which is insoluble in iron and hence goes into the slag if sufficient time is allowed. A great deal of the Al_2O_3 is entrained in the freezing iron, however, and hence the steel contains both Al_2O_3 as non-metallic inclusions and any excess aluminium is alloyed with the iron. If the steel is dissolved in dilute HCl, the Al_2O_3 nearly all remains insoluble, while the alloyed aluminium goes into solution. Hence, when desired, it is possible to make a thoroughly satisfactory separation of the aluminium present as oxide from that alloyed with the iron.

When a slightly acid solution of divalent iron and aluminium is boiled with the addition of a large amount of sodium phosphate the aluminium is precipitated as phosphate contaminated with small amounts of iron, chromium, zirconium and titanium, if these are present.

Aluminium is also very satisfactorily separated from iron by the use of phenylhydrazine. The solution must be slightly acid, and the iron divalent. Chromium, titanium, zirconium and thorium are precipitated with the aluminium hydroxide, Be, Mn, Co, Ni, Cd, Zn, Hg, Mg, Ba, Sr and Ca remaining in solution.

If the sample contains tungsten it must be removed as WO_3 by the usual methods.

Process of Analysis.—Dissolve 10 grams of the metal in 60 c.c. of concentrated HCl. Evaporate to dryness to separate SiO_2. Take up in HCl and filter and determine the SiO_2 as usual with the use of HF. Add to the residue left in the crucible, which will contain the Al_2O_3 which was in the iron as Al_2O_3, ½ gram of Na_2CO_3, fuse, dissolve the cake in water and add to the main solution. Dilute to 200 c.c., add ammonia until a slight, permanent precipitate appears, dissolve this by adding HCl drop by drop, add a slightly acid saturated solution of ammonia bisulfite with constant stirring until the solution smells strongly of SO_2. If the solution turns a deep red, add a little more HCl. Continue the addition of the bisulfite to the warm solution until no test for ferric iron is obtained with KCNS on a white plate. Now add 3 c.c. of phenylhydrazine with constant stirring until the alumina is precipitated.

As soon as the precipitate settles, filter and wash with water containing a small amount of phenylhydrazine sulfite until all iron is washed out. Dry, ignite in a platinum crucible and fuse the impure Al_2O_3 with 2 grams of sodium carbonate and ½ gram of KNO_3. Cool, digest the cake with hot water until thoroughly disintegrated, dilute to 50 c.c., filter and wash well with hot water. Iron and titanium remain on the filter paper while aluminium and chromium are in solution. (If the residue of iron and titanium is large in amount, the fusion and extraction should be repeated.) Add HCl to the filtrate until nearly neutral, then 2 c.c. in excess, boil to drive off CO_2, add 10 c.c. of 10 per cent sodium phosphate solution, heat to 60°C. and add ammonia until barely alkaline, allow to settle for two hours, filter, wash with hot water until chlorides are removed, dry, ignite in a porcelain crucible and weigh the $AlPO_4$. This weight multiplied by 0.2219 gives the weight of aluminium present.

Notes.—The phenylhydrazine bisulfite solution is made as follows: Add a cold saturated solution of SO_2 to a few cubic centimeters of phenylhydrazine until the precipitate which forms redissolves. The solution keeps well. For use, dilute 10 c.c. to 100 c.c. with water.

If the steel contains no chromium, the process as above described is easily carried out. If the steel is high in chromium, the final precipitate may contain some chromium, which will have to be separated by a second fusion with sodium carbonate and potassium nitrate. If the steel contains uranium, use ammonium carbonate instead of ammonia to precipitate $Al(OH)_3$.

The function of the ammonium bisulfite is to reduce the iron to a divalent form, as the trivalent iron precipitates by hydrolysis with the $Al(OH)_3$.

Instead of using phenylhydrazine, the same procedure may be used, except that 10 c.c. of saturated sodium phosphate and 5 grams of ammonium acetate are added.

REFERENCES:

HESS and CAMPBELL, *J. Am. Chem. Soc.*, **21**, **776.**
ALLEN, *Ibid.*, **25**, 421.
STEAD, *J. Soc. Chem. Ind.* (1889), 965.

ETHER METHOD

When the ether separation as given on pages 125, 129 is carried out, the aluminium passes into the aqueous solution with vanadium, manganese, nickel, etc. The aluminium can then be precipitated as above without having such a large amount of iron present.

Process.—Treat a 5- or 10-gram sample as directed on page 129 until the aqueous solution is separated from the ethereal solution. Then add 2 c.c. H_2SO_4, evaporate the solution until fumes of H_2SO_4 appear, dilute to 50 c.c. and precipitate the aluminium as directed above for the second precipitation.

CHAPTER XVIII

THE DETERMINATION OF URANIUM IN STEEL

Uranium is occasionally added to steel as an alloying element, especially in high-speed steels. The analysis depends upon the fact that uranium is separated along with vanadium, nickel, manganese, etc. from all except a small amount of the iron when the ether separation is made. The uranium is finally separated from iron and vanadium by means of sodium carbonate, in which solution uranium remains while iron and vanadium are precipitated.

Process of Analysis.—Proceed as directed on page 125 until the ether separation is made, and the aqueous solution is boiled until the volume is about 10 c.c. Add 30 c.c. of strong nitric acid and, if vanadium is present in large amounts, add enough iron to bring the iron content of the solution up to five times the amount of vanadium present. Again evaporate to 10 c.c., add 30 c.c. of HNO_3 and again evaporate to 10 c.c. to remove all HCl. Add 40 c.c. of HNO_3 and 5 grams of sodium chlorate and boil until 20 c.c. are left. Filter off MnO_2 through an asbestos mat in a Gooch crucible.

Dilute to 200 c.c. and add ammonium hydroxide *free from carbonate.* The iron, uranium and vanadium precipitate, leaving chromium in solution. If chromium be present in large amounts, the precipitate should be again treated with nitric acid and sodium chlorate and a second separation made.

Dissolve the precipitated hydroxides in 1:1 HNO_3, using 10 c.c., dilute to 20 c.c., neutralize with ammonia, add 20 c.c. excess, heat nearly to boiling, add 2 grams of sodium carbonate carefully, remove from the heat, stir for a minute and add 2 grams more of sodium carbonate. Heat to boiling, allow the precipitate to settle and filter off the oxides of iron and vanadium. Dissolve the precipitate in 10 c.c. of 1:1 HNO_3 and reprecipitate as above. Combine the filtrates, add HCl until acid and boil to expel all CO_2. Add ammonia *free from carbonate* until alkaline, boil for a few minutes, filter and wash with water slightly alkaline with ammonia. Dissolve the precipitate in 10 c.c. of 1:1 HNO_3, dilute to 20 c.c. and again precipitate the uranium with ammonia. The uranium precipitates as a lemon-yellow ammonium uranate ($(NH_4)_2U_2O_7nH_2O$). Filter, wash with water slightly alkaline with ammonia, ignite and weigh as U_3O_8.

Notes.—The purity of the residue may be tested by treating with HNO_3 (1.20 sp. gr.). Oxides of iron and chromium remain undissolved and can be filtered off and correction made. The vanadium goes into the filtrate and can be determined and correction made.

Sulfate solutions containing uranium may be reduced by the Jones reductor and the reduced solution titrated with permanganate, the uranium undergoing change from UO_2 to UO_3. This titration is quite accurate, provided iron and vanadium are absent.

The sodium carbonate precipitation of iron and vanadium also precipitates aluminium and titanium.

The precipitate of ammonium uranate is always impure if sodium or potassium salts are present, hence a double precipitation is necessary.

Uranium ores are analyzed practically the same as for steels except that it is not necessary to make the ether separation and the precipitate of iron and vanadium should in some cases be reprecipitated the third time. The uranium may be finally precipitated and weighed or the precipitate may be dissolved in 100 c.c. of 1:5 H_2SO_4 and reduced by the Jones reductor as directed on page 39.

REFERENCES:

U. S. Steel Corporation, "Methods for the Analysis of Alloy Steels."
HILLEBRAND, *Bull.* U. S. Geol. Survey, **78,** 47.
KERN, *J. Am. Chem. Soc.*, **23,** 685

CHAPTER XIX

THE DETERMINATION OF OXYGEN IN STEEL

This important determination has not received as much attention as it should have, as the properties of steel are considerably affected by the presence of considerable amounts of oxygen. The oxygen exists in the steel as oxides of iron, manganese, silicon, titanium, aluminium, etc. The method here given depends upon the reaction between the oxide of iron and hydrogen at a high temperature, with the formation of water vapor which is absorbed in phosphorus pentoxide and weighed.

Since hydrogen does not reduce the oxides of manganese, aluminium and silicon, the oxides combined with them are not determined with this method, that is, the method determines only the occluded oxygen and the oxygen combined with the iron and other easily reduced metals. However, when the metal is a very pure iron, containing only a few hundredths per cent of manganese and a trace of silicon, the result for oxygen obtained by this method must be fairly accurate. It is precisely in this kind of iron that the oxygen content must be closely watched. The oxides of easily reduced metals, such as copper, nickel and tungsten, could scarcely exist in steel, the oxides of the metals having a very high heat of oxidation, such as silicon, aluminium, chromium, vanadium, are undoubtedly present but are not reducible by hydrogen. The determination of oxygen in steel by the Ledebur method, using hydrogen, therefore, can only determine the oxygen present as iron oxide and probably this oxide when present as silicate is not completely reduced. The higher oxides of manganese, titanium and vanadium are reducible under the conditions of the method, but it is hardly conceivable that they are present. The oxygen which is present as occluded CO_2 and CO is largely included in the determination.

The determination depends upon the reaction $2FeO + H_2 = 2Fe + H_2O$, the water formed by the reaction being absorbed by phosphorus pentoxide and weighed.

The drillings used for the determination of oxygen are quite certain to have enough oxide formed on the surface, due to the heat generated during drilling, to have a profound effect upon the results, unless the drilling is done under oil.

The accurate determination of oxygen in steel requires the very greatest care and experience. The method as given below is the Ledebur method modified by the American Rolling Mill Company for practical furnace control.

Process of Analysis.—Drill the block of steel under oil until about 100 grams are obtained, pour off the oil and wash with benzol until all trace of oil is removed, dry thoroughly in a desiccator through which a current of air dried over sulfuric acid is passed. The sample should be used for the determination of oxygen as soon as possible after drying, since the steel slowly oxidizes.

For mill practice, where samples can be taken from bars, they should first be cleaned from all mill scale or surface oxide by the use of an emery wheel. The sample should then be placed in a milling machine which should be run at very slow speed in order to avoid oxidizing the millings. A light transverse cut should be taken entirely across the bar and the millings discarded in order to remove any oxidized cavities which were not removed by the emery wheel.

The sample should be the average of the entire cross-section if possible, as there is some difference in gas content between the interior and exterior portions of bars. The sample must be free from all dirt, and samples should not be ground in the vicinity where a sample is being milled, on account of the danger of contamination from finely divided particles of oxide of iron.

The millings should be removed from the sample by the use of a magnet, and placed in a dry glass-stoppered bottle. It is of the utmost importance that millings of uniform size be used for analysis, those passing a 20-mesh and remaining upon a 40-mesh sieve being selected. The millings should remain in the unstoppered bottle for half an hour in a desiccator containing concentrated sulphuric acid. A 30-gram sample is placed in a ½ × ½ × 6 in. platinum or pure iron boat (for cast iron use a porcelain boat), which is placed in the ⅞ × 30 in. silica tube *T*.

In most descriptions for determining oxygen by the Ledebur method, hydrogen is generated by the action of some acid upon zinc contained in a Kipp's generator. It has been found that hydrogen so prepared contains considerable carbon monoxide and carbon dioxide, whereas hydrogen produced by the electrolytic process and stored in tanks is practically free from these two gases, is much easier to handle and is cheaper.

Apparatus.—The apparatus used in making the oxygen determination is shown in Fig. 10.

A 4-liter Kipp generator may be used for generating the hydrogen. It should be charged with drillings of pure iron or mossy zinc, and dilute hydrochloric acid (1:1). Steel turnings should not be used in the generator, as the object is to generate the purest possible hydrogen. Hydrochloric is preferable to sulfuric acid. Electrolytic hydrogen is much better. After its formation, the hydrogen is purified and dried by passing through the usual train, as shown in the figure. It passes first over stick potash, and next through a 30 per cent potash solution. This solution in the second bottle should be renewed as soon as it shows a tinge of yellow, due to the presence of sulfides. The hydrogen next passes through concentrated sulfuric acid to dry it, and then enters a silica tube with ¼-in. bore, 30 in. in length, which contains a roll of platinum gauze or palladiumized asbestos. The ¼-in. tube lies on top of a 1 × 30-in. fused silica tube contained in a suitable 12-in. gas-blast furnace. It is better to preheat the hydrogen in a separate furnace.

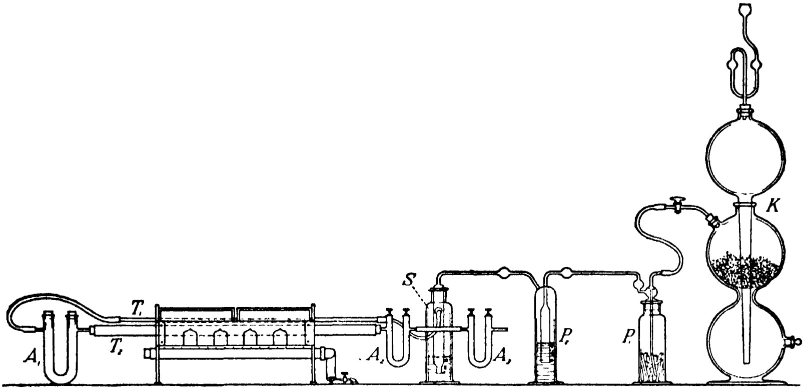

FIG. 10.

The object of the preliminary heating over platinum foil is to free the hydrogen from the small quantity of oxygen which it always contains. If this precaution is not taken, the results will be too high. The water formed in the small-bore tube is caught in a U-tube shown in the figure, which contains phosphoric anhydride opened up with glass wool. This drying tube has rubber stoppers. The connection is made with pure gum tubing and is permanent, the sample being introduced from the opposite end of the combustion tube. All rubber connections should be made tight, as directed on page 328.

Blanks should be run from time to time to make sure that the apparatus is in good order and everything working properly. Samples should not be introduced into or removed from the combustion tube when it is more than hand-hot, but silica tubes may be quickly cooled with perfect safety by turning off the gas and allowing the cold-air blast to play on the tube.

Process of Analysis.—Weigh 20 or 30 grams of finely divided borings into a silica boat ½ × ½ × 6 in. The boat with its charge is quickly inserted into the combustion tube at the right end and pushed to the middle zone by means of a rod of suitable length. The stream of hydrogen should be passing freely when the tube is opened for the insertion of the sample. After the stopper is replaced, the weighing tube and guard tube are finally connected up with pure gum tubing. The weighing tube is a 4-in. U-tube, with ground glass stoppers, containing phosphoric anhydride opened up with glass wool. The guard or trap tube is similarly charged and is intended to prevent the drawing back of moisture from the air of the laboratory. After the apparatus is all connected and in good order, the pure dry hydrogen should be allowed to sweep through a few minutes until all traces of air are removed from the entire system. The gas is then lighted, the blast turned on and the temperature run up to a yellow heat, about 1,000°C. This heat is maintained for 30 minutes while the hydrogen is passing through the apparatus at the brisk rate of about 100 c.c. per minute. After the combustion is completed, the gas is turned off the furnace, leaving the blast playing upon the hot tube. The stream of hydrogen should continue to pass until the tube is cool enough to bear the hand upon it.

Immediately after the tube is cool enough, the weighing tube, with its guard tube, is disconnected and connected with a suitable aspirator, so as to suck out the hydrogen gas and replace it with air dried over P_2O_5. A suitable aspirator consists of a 4-liter aspirator bottle filled with water. The upper tubular of the bottle is guarded with a calcium chloride tube to which the weighing tube is connected. A gas washing bottle containing concentrated sulfuric acid follows the phosphoric anhydride tube which is connected to the other side of the weighing tube. Place the weighing tube in the balance with an exactly similar tube and allow them to remain for 15 minutes to come to the temperature of the balance and to attain the same degree of moisture on the surface of the glass. Weigh, using the other tube as a counter poise. The weighing tube should, of course, be weighed in exactly the same way at the beginning of he determination. The increase in weight is H_2O produced by the determination. Results ought to check within 0.003 per cent. Blank determinations and proper corrections must be made.

Notes on the Process.—The aspirator may be roughly calibrated by allowing about 500 c.c. of water to run out of the lower tubular of the aspirator. A sufficient quantity of perfectly dry air is drawn through to displace all the hydrogen thoroughly. After all is ready, the weighed tube is closed by its glass stop-cocks, disconnected from its guard tube and placed in a desiccator for 15 minutes before being weighed. Eight-ninths of the increased weight of the tube is oxygen. The blanks on the apparatus establish the average correction to be subtracted from the weight found. The correction on an apparatus in good order should not exceed 2 mg. On damp days the blank is usually a little higher than when the air is dry.

If the stop-cocks on the weighing tube are ground so as to fit very tightly, it is not necessary to displace the hydrogen with air. If the cocks do not fit very tightly, some hydrogen will diffuse out.

In charging the weighing tube with phosphoric anhydride and glass wool, take care to remove any specks of phosphoric anhydride from the upper portions of the tube.

The following points should be given careful attention in order to attain the highest degree of accuracy:

Samples must be clean, absolutely dry and free from oil. They should be cut, preferably with a milling machine tool running at a low rate of speed. The samples must not heat in cutting. Sheet samples are first cleaned from oxide on an emery wheel, avoiding heating as much as possible. The sheet should be milled on the edge.

Whenever possible, samples should be cut from bars which are first cleaned by a superficial cut with the milling tool. Extreme care must be taken in the preparation of the sample.

The entire apparatus must be kept to the top notch of cleanliness, tightness and general good order. Blanks should be run frequently. Analyses should be in duplicate whenever the results are to be used as a basis for specification. The most extreme care should be taken to exclude all oxygen from the sample and apparatus except that which it is the object to determine.

REFERENCES:

CAIN and PETTIJOHN, U. S. Bureau of Standards, *Techologic Paper* 118.

WALKER and PATRICK, *J. Ind. Eng. Chem.* (Nov. 1912), 799.

The American Rolling Mills Company, "Analysis of Iron and Steel."

Determination of Hydrogen in Steel.—Hydrogen is determined in exactly the same manner as described for oxygen, except that pure oxygen is used and the temperature of the combustion tubes is kept at about 800°C., and the oxygen is passed through at the rate of 25 c.c. per minute for 30 minutes. The hydrogen in the steel is oxidized to H_2O and weighed as described under oxygen.

CHAPTER XX

THE DETERMINATION OF NITROGEN IN STEEL

It is well known that nitrogen in steel causes brittleness and effects the thermal transformation points. The nitrogen is present in steel as occluded gaseous nitrogen and as nitrides of iron, titanium and vanadium. When ordinary steel is unusually high in nitrogen, as, for instance, when heated in the presence of ammonia or cyanide, the presence of nitrogen as nitride is clearly evident as needle-like crystals when examined by the microscope.

The method most widely in use for the determination of nitrogen is Langley's. This method does not determine the total nitrogen in the steel. Occluded nitrogen and insoluble nitrides and cyanamides are not included. Steels which have been treated with titanium or vanadium are apt to have insoluble nitrides.

The method is useful, however, in ordinary steels and irons, since it appears that the corrosion of steel and iron is hastened by the presence of nitrogen as iron nitride, which is determined by this method.

The following method is the one devised by Allen and perfected by Langley as it is used by the American Rolling Mill Company. It depends upon the fact that when a steel is dissolved in hydrochloric acid the nitrogen which was present as nitride is retained by the acid present as ammonium chloride. The solution is then made alkaline by sodium hydroxide and the ammonia distilled off. The distilled ammonia is then treated with Nessler's reagent with which it produces a brown precipitate of enormous coloring power, so that the minutest trace of ammonia can be recognized by the formation of a distinct yellow color. The reaction is

$$2HgK_2I_4 + 3KOH + NH_4OH = 3H_2O + 7KI + OHg_2NH_2I,$$

the mercury compound being the colored precipitate.

Since the reaction is so very delicate, the utmost care must be used to see that no ammonia is allowed to get into the solutions used from the air, and especially prepared water and chemicals must be used. Even then it is imperative that blanks be frequently run. The determination must be made in a room in which there is no (or the least possible) quantity of free ammonia or ammonium salts in the air.

The reagents required are:

Hydrochloric Acid of 1:1 Specific Gravity, Free from Ammonia.—This may be prepared by distilling pure hydrochloric acid gas into distilled water free from ammonia. To do this, take a large flask fitted with a rubber stopper carrying a separatory funnel tube and an evolution tube. Place in the flask strong hydrochloric acid, connect the evolution tube with a wash bottle connected with a bottle containing the distilled water. Admit strong sulfuric acid free from nitrous acid to the flask through the funnel tube, apply heat as required and distill the gas into the prepared water.

Test the acid by admitting some of it into the distilling apparatus, described further on, and distilling it from an excess of pure caustic soda, or determine the amount of ammonia in a portion of hydrochloric acid of 1:1 specific gravity, and use the amount found as a correction.

Solution of Caustic Soda.—Dissolve 300 grams of fused caustic soda in 500 c.c. of water, and digest it for 24 hours at 50°C. with a copper-zinc couple prepared by rolling together about 6 sq. in. each of zinc and copper foil.

Nessler Reagent.—Dissolve 35 grams of potassium iodide in a small quantity of distilled water, and add a strong solution of mercuric chloride little by little, shaking after each addition, until the red precipitate dissolves. Finally, the precipitate formed will fail to dissolve; then stop the addition of the mercury salt and filter. Add to the filtrate 120 grams of caustic soda dissolved in a small amount of water, and dilute until the entire solution measures 1 liter. Add to this 5 c.c. of saturated aqueous solution of mercuric chloride, mix thoroughly, allow the precipitate formed to settle and decant or siphon off the clear liquid into a glass-stoppered bottle.

Standard Ammonia Solution.—Dissolve 0.0382 gram of ammonium chloride in 1 liter of water; 1 c.c. of this solution will equal 0.01 mg. of nitrogen.

Distilled Water Free from Ammonia.—If the ordinary distilled water contains ammonia, redistill it, reject the first portions coming over, and use the subsequent portions, which will be found free from ammonia. Several glass cylinders of colorless glass of about 160 c.c. capacity are required.

The best form of distilling apparatus consists of an Erlenmeyer flask of about 1,500 c.c. capacity, with a rubber stopper carrying a separatory funnel tube and an evolution tube, the latter connected with a condensing tube, around which passes a constant stream of cold water. The inside tube, where it issues from the condenser, should be sufficiently high to dip into one of the glass cylinders placed on the working table.

Process of Analysis.—Place 40 c.c. of the caustic soda, which has been treated with the copper-zinc couple, in the Erlenmeyer flask, add 500 c.c. of water and about 25 grams of tin foil to prevent bumping, and distill until the distillate gives no reaction with the Nessler reagent. While this part of the operation is in progress, dissolve 3 grams of the carefully washed drillings in 30 c.c. of the prepared hydrochloric acid, using heat if necessary. Transfer the solution to the bulb of the separatory funnel tube, and when the soda solution is free from ammonia, very slowly drop the ferrous chloride solution into the boiling solution in the flask until it is all in. Heat to boiling. When about 50 c.c. of water has been collected in the cylinder, remove it and substitute another cylinder. Place 1½ c.c. of the Nessler reagent in a cylinder, dilute the distillate to 100 c.c. with the special distilled water and pour it into the cylinder containing the Nessler reagent. Take another cylinder, place therein 1½ c.c. of the Nessler reagent and 100 c.c. of the special distilled water to which 1 c.c. of the ammonium chloride solution has been added, and compare the colors of the solutions in the two cylinders. If the solution in the cylinder containing the ammonium chloride solution is lighter in color than that in the cylinder containing the distillate, place 1½ c.c. of the Nessler reagent in another cylinder, pour into it 100 c.c. of water containing 2 or more c.c. of the ammonium chloride solution and repeat this operation until the colors of the solutions in the two cylinders correspond after standing about 10 minutes. When about 100 c.c. have distilled into the second cylinder, replace it and test as before. Continue the distillation until the water comes over free from ammonia, then add together the number of cubic centimeters of ammonia solution used, divide the sum by 3, and each 0.01 mg. will be equal to 0.001 per cent of nitrogen in the steel.

CHAPTER XXI

THE DETERMINATION OF SPELTER AND TIN PLATE COATING

The following method is recommended by the American Rolling Mill Company:

The method for determining the weight of spelter coating consists of dissolving it in HCl containing a small amount of antimony chloride. Antimony chloride appears to hasten the solution of the coating, and after the coating has dissolved a thin film of antimony plates on the surface of the base metal and retards the solution of iron or steel. Experiments have shown that sheet steel 2¼×2¼ in. which loses 50 mg. in five minutes in cold hydrochloric acid (sp. gr. 1.20), will lose in that time only 1 mg. in the same acid containing 80 mg. of antimony per 105 c.c. of acid.

In this method the metal is immersed in the acid only one minute, which is long enough to dissolve several grams of coating, yet the amount of iron or steel dissolved is negligible. The small amount of antimony which plates on the surface of the sample can easily be removed by scrubbing under running water. This method is rapid and accurate and a determination can be made in less time than is occupied in making the Preece test.

Process for Sheets.—For determining the weight of coating on galvanized sheets, cut three samples 2¼×2¼ in. from a strip cut from the middle of the sheet. The three samples should be weighed together and immersed singly for one minute in 100 c.c. of HCl (sp. gr. 1.20), to which has been added 5 c.c. of antimony chloride prepared by dissolving 20 grams of antimony trioxide in 1,000 c.c. of HCl (sp. gr. 1.20). The same 100 c.c. of HCl can be used for at least five samples. Five cubic centimeters of the antimony chloride, however, should be added for each sample, on account of the antimony being removed from the solution by the iron.

Wash and scrub the samples under running water, dry with a towel, lay in a warm place for a few seconds and weigh. Each gram of loss in weight corresponds to 1 oz. of coating per square foot.

Wire.—A small section of the galvanized wire should be stripped in hydrochloric acid containing antimony chloride. The diameter of the black wire should then be carefully measured in order to determine the length of wire, such that the number of grams of coating will represent the number of ounces per square foot of surface. In the lighter wires, however, it will be found convenient to use some fraction of these lengths.

The method of making the test is very similar to that outlined for galvanized sheets, except that the wire is first cleaned with carbon tetrachloride or gasoline, and after being carefully weighed is placed in a tall glass cylinder containing hydrochloric acid (sp. gr. 1.20), to which has been added from 2 to 3 c.c. of antimony chloride solution of the same strength as used on galvanized sheets. The reason for using one-half the amount of antimony chloride in the case of wire is on account of taking one-half the area. As previously stated, the coating on galvanized sheets is expressed in ounces per square foot, considering one side only, when in reality this amount of coating represents 2 sq. ft. of surface. After immersing the entire length of wire for one minute it will be found convenient to pour the acid solution into another tall cylinder in order to facilitate removing the wire. The wire is then scrubbed under running water, wiped, thoroughly dried in a warm place for a few seconds and again weighed. Each gram lost corresponds to 1 oz. of coating per square foot. For direct comparison with the weight of coating as expressed on galvanized sheets, this figure should be doubled.

ANALYSIS OF TIN AND TERNE PLATE AND LEAD-COATED SHEETS, METHOD OF THE AMERICAN ROLLING MILL COMPANY

Several samples exactly 2×2 in. should be taken for analysis. Clean thoroughly with carbon tetrachloride or gasoline and weigh. A 400-c.c. Jena glass beaker has been found the most convenient for this test. It has been found that 20 c.c. of concentrated sulfuric acid is sufficient for each 2×2-in. piece.

If four pieces are taken, however, 60 c.c. of sulfuric acid will be sufficient. Place the requisite amount of acid in the beaker and heat to at least 250°C. Wrap a stiff platinum or nickel wire around one of the 2×2-in. pieces so that it can be placed in the acid in a horizontal position. Immerse the piece in the hot acid for exactly one minute. Transfer the piece to another 400-c.c. beaker containing 25 c.c. of distilled water and rub the surface of the sample while washing with about 50 c.c. more distilled water, using a wash bottle for this purpose. Dry the sample thoroughly and reweigh. The loss in weight represents the coating and some iron. Repeat this operation for each sample, collecting all rinsings in a beaker, and reserve for analysis.

The iron which has dissolved is determined as follows: The sulfuric acid is carefully poured into the beaker containing the washings from the 2×2-in. pieces. This solution is cooled and poured into a volumetric flask. Then 25 per cent by volume of concentrated hydrochloric acid is added and the flask filled to the mark with distilled water. If four pieces have been taken for analysis, a 500-c.c. volumetric flask will be required. Use a proportionately smaller flask if less than four samples are analyzed. Mix thoroughly, and transfer 100 c.c. of the solution to a 300-c.c. Erlenmeyer flask. Add a solution of tenth-normal permanganate until iron and tin are oxidized, which is indicated by the appearance of a permanent straw color. No account is taken of the amount of permanganate used. Heat to boiling and reduce carefully with stannous chloride. Cool and pour into a 1,000-c.c. beaker containing 500 c.c. of distilled water and 25 c.c. of saturated solution of mercuric chloride, stir vigorously, add 50 c.c. of the titrating mixture of phosphoric acid and manganese sulfate and titrate with tenth-normal permanganate to pink color. The amount of iron which has thus been determined is subtracted from the total weight lost in sulfuric acid; the remainder is coating. It is very often unnecessary to make an analysis of the coating, the object being merely to determine the weight.

There are several ways of expressing the weight of the coating; we prefer to express it in ounces per square foot. By knowing the number of square feet in a box of tin plate or a case of terne plate there is no confusion in converting the ounces per square foot to pounds per box or case. The coating on tin plate is sometimes expressed in pounds per box of 112 sheets 14×20 in. This figure can be obtained by multiplying the number of grams of coating of each 2×2-in. piece by 17.29. If it is desired to express the coating on terne plate in pounds per case of 112 sheets 20×28 in., then multiply the number of grams of coating on each 2×2-in. piece by 34.57. The average of the several pieces represents the weight of coating.

If the determination of tin and lead is desired in the sheet, proceed as follows: Place another 100 c.c. of the sulfuric acid solution containing the coating in a 300-c.c. Erlenmeyer flask. Whether lead sulfate is or is not removed with this 100 c.c. does not influence the accuracy of the tin analysis. Add 50 c.c. of concentrated hydrochloric acid, 2 grams of iron drillings and 1 gram of finely ground antimony. Connect flask with a one-hole stopper containing a glass tube bent twice at right angles, the end of which projects into a beaker of water. Heat until all iron is dissolved, boil five minutes and replace the beaker containing the water with one containing an 8 per cent solution of bicarbonate of soda prepared from boiled distilled water. Remove the flask from the hot plate and allow the soda water to flow back into the flask while cooling same with tap water. When cold, add a few cubic centimeters of starch solution and titrate to permanent blue color with tenth-normal iodine solution. One cubic centimeter equals 0.00595 gram of tin. The amount of tin found is subtracted from the weight of coating which has been determined by loss in sulfuric acid, and after the iron correction has been made the remainder is lead.

Notes.—For details of the chemistry and method see the determination of tin in ores, page 216, and the analysis of bearing metals, page 195.

In the determination of tin in tin plate it is only necessary to determine the loss in sulfuric acid, and then to determine the iron which has been dissolved, the remainder being tin.

Heavily coated lead sheets may require twice as much acid and a temperature of 300°C. to remove the coating completely in one minute.

CHAPTER XXII

THE ANALYSIS OF SPELTER

Spelter is the commercial name for the ordinary zinc of commerce. The chief impurities in spelter are lead, iron and cadmium.

Determination of Lead.—Lead may be determined with equal accuracy electrolytically or by weighing as $PbSO_4$. Weigh 8.643 grams of the cuttings, transfer to a 400-c.c. beaker and add 60 c.c. of 1:1 HNO_3. When action is complete, boil the solution for a few minutes, dilute to 150 c.c. and electrolyze, using gauze electrodes of about 2½×2½ in. Use a current of 3 to 5 amp. for 45 minutes to an hour and a half. Wash down the cover glass and the sides of the beaker occasionally with a little water. At the end of the time mentioned above immerse the electrodes ¼ in. deeper and see if more lead is deposited on the freshly immersed surface. If not, the electrolysis is complete. Wash the anode three or four times with distilled water, then with alcohol, dry in an oven at 210°C., cool and weigh. The weight of the deposited PbO_2 in milligrams divided by 100 gives the percentage of lead in the sample.

Notes.—The empirical factor weight (8.634 grams) is used instead of the theoretical one (8.660 grams), as dried PbO_2 contains some included water, not entirely expelled.

Before electrolyzing, the beaker should be covered with split watch-glasses to prevent loss by spraying. The time required for complete deposition is usually 30 to 45 minutes. For small amounts of lead, 30 minutes are sufficient. The washing should be done immediately, as the deposit of PbO_2 tends to dissolve. The PbO_2 deposit can be readily removed by immersing in hot dilute HNO_3 containing some oxalic acid. Any manganese in the sample will be deposited as MnO_2.

Determination of Iron.—Dissolve 25 grams of the sample with 125 c.c. of HNO_3 in an Ehrlenmeyer flask, covering the sample first with a little water. Boil, dilute to 300 c.c., add 10 c.c. of HCl and then ammonia until the precipitated $Zn(OH)_2$ has redissolved. Boil, let settle and filter on an 11-cm. filter paper. Wash with dilute ammonia water and then with hot water until free from chlorides. Dissolve the precipitate from the paper with hot H_2SO_4 (1:4), add 40 c.c. of H_2SO_4 (1:1), cool and pass through a Jones reductor. Wash out the reductor first with 150 c.c. of dilute H_2SO_4 and then with 100 c.c. of distilled water and titrate with a standard $KMnO_4$ solution.

Notes.—A filter paper which will retain $Fe(OH)_3$ and filter rapidly should be used. Whenever the amount of iron is at all large, or when great accuracy is demanded, a second precipitation of $Fe(OH)_3$ should be made by dissolving the precipitate on the paper in hot dilute HCl, adding ammonia water and filtering, in order to remove all traces of nitrates.

The reductor should be clean, preferably washed out with 150 c.c. of dilute H_2SO_4 and 100 c.c. of water first. If, before passing through the reductor, a large amount of $PbSO_4$ is present, it is well to filter it off so as to prevent it from clogging the reductor. A small quantity of liquid should always be left in the reductor funnel, and air should never be allowed to enter the body of the reductor. A blank determination should be made.

Cadmium Determination.—When spelter is dissolved in acids like HCl and H_2SO_4, the cadmium remains undissolved as long as there is still undissolved zinc. In this way the cadmium from a large sample of spelter is concentrated to a residue high in cadmium and low in zinc.

Dissolve 25 grams of drillings with 250 c.c. of water and 55 c.c. of HCl (sp. gr. 1.20). When action has almost ceased, add more acid with stirring, using about 2 c.c. at a time until all but about 2 grams of zinc has been dissolved. Filter, transferring some of the undissolved zinc to the filter and wash twice with water. Wash the undissolved matter on the filter paper back into the beaker, cover and dissolve with 20 c.c. of 1:1 HNO_3, add 20 c.c. of 1:1 H_2SO_4 and evaporate until fumes of SO_3 appear. Add 100 c.c. of water, boil and allow to stand until all $PbSO_4$ settles. This should be given several hours or preferably overnight. Filter, wash three or four times with water containing a little H_2SO_4, dilute the filtrate to 400 c.c., add 10 grams of NH_4Cl and pass H_2S

gas through for one hour. If CdS does not appear soon, add a few drops of ammonia. Allow the sulfide to settle and filter the impure CdS through a Gooch crucible. Transfer to a 200-c.c. beaker, add 60 c.c. of 1:5 H_2SO_4 and boil for 30 minutes, filter, wash the sulfides of copper, antimony, etc., dilute the filtrate to 300 c.c., add 5 grams of NH_4Cl and again precipitate with H_2S. Filter the CdS and wash with water containing H_2S. Transfer the precipitate to a small evaporating dish, dissolving what remains on the filter paper with hot 1:2 HCl, catching the washings in the evaporating dish, add 10 c.c. of 1:1 H_2SO_4 and evaporate until copious fumes of SO_3 are evolved. Place the dish in a muffle and heat gradually until a temperature of 500° C. is reached (a barely visible red). Cool and weigh as $CdSO_4$.

Notes.—If the Cd is unusually large, a third precipitation with H_2S may be necessary. Instead of weighing the Cd as sulfate, the sulfate may be dissolved, made slightly alkaline with KOH, KCN added until the solution clears up and the cadmium then precipitated electrolytically.

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CHAPTER XXIII

ANALYSIS OF ALUMINIUM AND ALUMINIUM ALLOYS

The usual impurities in aluminium are silicon and iron. Copper, manganese, zinc, nickel, tin and some other metals are added to obtain specific properties. Silicon is also used to strengthen aluminium.

Determination of Silicon.—Dissolve 1 gram of the drillings in a mixture consisting of 20 c.c. of water, 6 c.c. of H_2SO_4, 15 c.c. of HCl and 5 c.c. of HNO_3. When solution is complete, evaporate in a casserole, finally raising the temperature until fumes of SO_3 are copiously evolved, cool, add 100 c.c. of water and a few c.c. more of H_2SO_4 and heat until sulfates are all dissolved. Filter, wash until the filtrate is no longer acid to litmus, ignite and weigh the SiO_2. Calculate to silicon by multiplying by 0.4693.

Aluminium sometimes contains silicon in the "graphitic state." This graphitic silicon does not oxidize to SiO_2, nor is it volatile with HF. Hence, if the above weighed material is treated with HF, then evaporated and ignited again, the residue is the graphitic silicon. This graphitic silicon may then be treated with a mixture of HNO_3 and HF, which attacks the graphitic silicon.

Determination of Iron.—Cool the filtrate obtained from the SiO_2 and reduce the iron and titrate with permanganate as directed on page 36.

Analysis of Aluminium Alloys.—Metallic aluminium is readily attacked by hot concentrated NaOH. Place 1 gram of the drillings in a porcelain dish, add just enough water to cover the drillings and 5 grams of solid NaOH. When violent action has ceased, dilute to 200 c.c. with hot water and boil until solution is complete. Filter while hot and wash the residue until free from alkali. The aluminium and most of the zinc dissolve, while other metals remain in the metallic state.

Determination of Copper.—Dissolve the residue in 5 c.c. of hot 1:1 HNO_3, dilute to 50 c.c. and add ammonia until barely alkaline, then add HCl until slightly acid. Dilute to 150 c.c. and precipitate the copper with H_2S, filter and wash free from acid, ignite in a porcelain crucible and dissolve the CuO in 2 c.c. of HNO_3. Determine the copper by the iodide or sulfocyanate methods given on pages 229 and 244.

Determination of Manganese.—Treat 1 gram of the sample exactly as directed on page 84 for the bismuthate method.

Determination of Calcium and Magnesium.—Dissolve the sample with NaOH as above directed. Dissolve the metallic residue in 40 c.c. of 1:1 HCl and a few drops of HNO_3, neutralize with ammonia, add 5 c.c. excess, precipitate with H_2S and filter. In the filtrate, determine the calcium and magnesium as directed on page 381.

Determination of Nickel.—Decompose the sample with NaOH as above directed and dissolve the residue with as small an amount of hot 1:1 HNO_3 as possible. Dilute to 100 c.c., add NaOH solution until alkaline, then HCl until acid and 10 c.c. in excess. Determine the nickel as directed on page 123.

Determination of Zinc.—Dissolve a 1-gram sample with NaOH as above directed, dissolve the metallic residue with a little hot HNO_3 1:1, filter, wash with hot water and make alkaline with NaOH, boil for several minutes and filter off the iron, chromium, manganese, nickel, etc. hydroxides. Add the filtrate to the main solution and pass H_2S through the boiling hot solution. The zinc precipitates as ZnS. Filter through a double filter but do not wash. Dissolve the precipitate with the least possible amount of hot 1:1 HCl, catching the filtrate in the beaker in which the precipitation was made. Determine the zinc by the ferrocyanide method as directed on page 204.

Determination of Titanium.—Dissolve a 1-gram sample as directed above with NaOH, dilute to 200 c.c., heat to boiling, filter and wash well. Burn in a platinum crucible until all the carbon is gone, fuse the residue with 2 grams of $KHSO_4$, cool, dissolve in water containing 2 per cent of H_2SO_4 and determine the titanium colorimetrically as directed on page 149.

Determination of Chromium.—Proceed exactly as directed for chromium in alloy steels.

Determination of Vanadium.—Proceed exactly as directed for vanadium in alloy steels.

Determination of Uranium.—Dissolve a 1-gram sample in NaOH as previously directed, with the exception that the NaOH should be previously treated with $Ba(OH)_2$. Filter off the residue, wash into a beaker and digest with 10 c.c. of hot 1:1 H_2SO_4. Filter and wash with hot water. Neutralize the filtrate with 20 per cent Na_2CO_3 solution, add 5 c.c. of H_2O_2 and 30 c.c. more of 20 per cent Na_2CO_3 solution. Boil for five minutes and filter off the iron. Carefully neutralize the filtrate with 1:1 H_2SO_4 and add 10 c.c. excess, boil off the CO_2 and add 20 c.c. of 20 per cent solution of ammonium phosphate. Add ammonia until barely alkaline, boil for 10 minutes, filter and wash with hot water a few times. Dissolve the precipitate on the filter with hot 1:4 H_2SO_4, wash and reduce the uranium with a Jones reductor. Titrate the reduced solution promptly with standard $KMnO_4$. The iron value of the permanganate multiplied by 2.133 gives the uranium.

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CHAPTER XXIV

THE ANALYSIS OF COPPER

The properties of copper are greatly affected by the presence of small amounts of impurities. The most common impurities are arsenic, antimony, oxygen, bismuth, lead, iron, sulfur. Also silver and gold are often present in considerable amounts, while silicon, aluminium, nickel, cobalt, selenium, phosphorus and tellurium may be present.

The following method for arsenic and antimony is as described by Heath. It depends upon the precipitation of the antimony and arsenic from the solution of the copper by adding a sufficient amount of ferric salt and then NH_4OH. The ferric hydroxide carries down with it the arsenic and antimony in combination with the iron. The arsenic and antimony are separated from the iron by hydrogen sulfide, the sulfides are dissolved in sodium sulfide and the arsenic and antimony oxidized to pentavalent form by fuming nitric acid. Arsenic is separated from antimony by precipitating it out as sulfide from 2:1 hydrochloric acid solution in which antimony sulfide is soluble.

Copper when present in large quantities is always best determined electrolytically, but, since most of the impurities in copper are precipitated more or less completely with copper when it is deposited electrolytically, it is necessary to purify the solution from which copper is to be deposited.

Determination of Copper.—Dissolve a 5-gram sample in 42 c.c. of the "Assay Solution" and evaporate until all the HNO_3 is expelled. Redissolve in 70 c.c. of water and add 3 c.c. of ferric nitrate solution (1 c.c. = 0.01 gram of iron). Transfer the solution to a lipped beaker and place the original beaker under a funnel fitted with a small filter paper. Precipitate the iron from the hot liquid by ammonia, filter and wash well. Place the solution on a hot plate to concentrate, reprecipitate the hydroxide from dilute H_2SO_4 in a very small volume of solution and add the filtrate to the main solution. Reprecipitate the hydroxide once more from dilute H_2SO_4, filter, wash thoroughly and add the filtrate to the main solution. Make the solution acid with dilute H_2SO_4 and add 2 c.c. of HNO_3 (sp. gr. 1.42).

Dilute to 150 c.c. in a 250-c.c. beaker and place the electrodes in the beaker so that the cathode is completely immersed. The cathode must be of platinum gauze and should be made of 50 meshes per lineal inch, with a total surface of about 100 sq. cm. Connect the electrodes to storage cells or other source of direct current and electrolyze, using a current of 2 to 4 amp. until gas commences to be evolved on the cathode. This will require not less than four hours. During the electrolysis the beaker must be covered with a split cover glass, otherwise considerable amounts of the solution will be lost by spraying. When gasing starts at the cathode, reduce the current to about 0.4 amp., wash the sides of the beaker and the cover glass with water and continue electrolysis. When it is thought that the copper is completely precipitated, pipette 1 c.c. of the solution, place on a porcelain plate and test with a few drops of fresh H_2S water. If no discoloration occurs, the electrolysis is complete.

Without interrupting the current, siphon off the acid solution, at the same time filling the beaker with distilled water. Remove the cathode quickly and rinse it in distilled water and two successive baths of alcohol. An experienced operator can quickly remove a cathode and immerse it in water without loss. Throw off the excess alcohol by a quick motion of the hand and ignite the remainder by bringing the cathode quickly to the flame of an alcohol lamp; then keep the cathode moving continually while the alcohol burns. Weigh as metallic copper.

"Assay Solution."—Mix 300 c.c. of H_2SO_4 (sq. gr. 1.84), 210 c.c. of HNO_3 (sp. gr. 1.42) and 750 c.c. of distilled water.

Notes.—If the copper is highly refined copper, the removal of arsenic and antimony by precipitation of iron hydroxide may be omitted and the solution of the copper in the "Assay Solution" electrolyzed directly after dilution to 150 c.c.

The accuracy of the determination should be within 0.015 per cent.

Silver, which may be present, is deposited with the copper.

A few thousandths of a per cent of the copper may remain undeposited. This may be determined after evaporation to 50 c.c. by neutralizing with ammonia, then making slightly acid with HCl and precipitating with H_2S. The CuS is dissolved in nitric acid, then electrolyzed from a small solution.

Determination of Arsenic, Antimony and Bismuth.—Dissolve 25 grams of the drillings in a 600-c.c. beaker with 110 c.c. of nitric acid (sp. gr. 1.42). Dilute to 300 c.c. and add a solution of 2 grams of c.p. ferric sulfate made from c.p. crystallized ferrous sulfate. Heat nearly to boiling and add NH_4OH until the iron is precipitated and the copper salts redissolved. This will take about 175 c.c. Heat to boiling, let settle a half hour on a hot plate and filter on a 15-cm. ashless paper. If bismuth is to be determined, add 2 grams of ammonium carbonate and 5 c.c. of saturated sodium phosphate solution after the iron is precipitated. If the copper contains more than 0.1 per cent of arsenic and antimony, add more of the ferric sulfate to the acidified filtrate and again precipitate with NH_4OH, filter and wash both precipitates well with hot 1:10 NH_4OH. Redissolve the precipitate or precipitates with dilute sulfuric acid, precipitate again with NH_4OH, filter and wash well.

Dissolve the ferric hydroxide with hot dilute sulfuric acid containing 5 per cent of hydrochloric acid and precipitate in the cold the arsenic antimony and bismuth with hydrogen sulfide, passing the gas through for 15 minutes. Stopper the flask and let settle overnight. In the morning pass hydrogen sulfide through again, filter on a small filter paper and wash with slightly acid hydrogen sulfide water.

Transfer the paper and contents to a small beaker and dissolve the sulfides of antimony, arsenic and tin with hot sodium sulfide, digesting until they are all dissolved. Use as little sodium sulfide as possible. Filter and wash with slightly alkaline hydrogen sulfide water. Bismuth sulfide remains on the filter.

To the filtrate add 0.2 gram of sodium hydroxide, evaporate to dryness on a steam plate, treat the residue with 20 c.c. of strongest fuming nitric acid and digest until the sulfur is all dissolved. Evaporate to dryness again.

Dissolve the residue in 35 c.c. of hydrochloric acid containing two parts of hydrochloric acid (sp. gr. 1.2) to one of water, adding a crystal of tartaric acid. Pass hydrogen sulfide through the cold solution until the solution is saturated whereupon the arsenic precipitates. Allow to settle a short time, filter on an asbestos mat, and wash with acid of the same strength as the solution. Wipe out any sulfide adhering to the side of the beaker with asbestos. As soon as the mat is washed well, the beaker is removed and the acid removed from the mat with H_2S water. Test the filtrate with more hydrogen sulfide gas. Keep the filtrate for the antimony.

Digest the mat with the sulfides in a small beaker with fuming nitric acid, dilute with 1½ times its volume of water and filter, wash and evaporate to dryness with 0.1 to 0.5 gram of sodium nitrate, according to the amount of arsenic present.

Dissolve the residue in 5 c.c. of cold water, 10 drops of hydrochloric acid and 0.1 gram of tartaric acid. Filter through a small paper and wash with the smallest amount of water possible. Make slightly alkaline with NH_4OH, when the volume should not be more than 12 c.c. Add 3 c.c. of magnesia mixture, make up to 20 c.c. with strong NH_4OH and stir five minutes. If the amount of arsenic is excessive add more precipitant and increase the volume to 30 c.c., one-third of which is NH_4OH.

Allow to stand over night in a cool place, filter on a 3-cm. filter paper and wash with a fine jet of 1:3 NH_4OH until free from chlorine. Dry the paper in an oven, crumble out the arsenate on a glazed paper and put the paper in a porcelain crucible. Add a few drops of saturated ammonium nitrate and char the paper very carefully, add more nitrate and again heat carefully until the paper is consumed without giving an odor of arsenic. Add the rest of the arsenate, ignite at a full red-heat and weigh. Or filter the arsenate on a small weighed Gooch filter, wash well, ignite and weigh as $Mg_2As_2O_7$, which contains 48.27 per cent As.

The magnesia mixture should be free from lime and should not be used after it has attacked the glass of the bottle. It is made of one part of magnesium sulfate, four of ammonium chloride, eight of water and four of ammonia (sp. gr. 0.90).

Instead of determining the arsenic gravimetrically, it may be titrated. Transfer the solution of arsenic sulfide in fuming nitric acid to a Kjeldahl flask, add 15 c.c. sulfuric acid and 3 grams of $KHSO_4$ and evaporate to fumes for 15 minutes. Cool, add 0.5 gram tartaric acid and fume until colorless. Cool, dilute to 200 c.c. and add NH_4OH until just alkaline, then make just acid, add 3 drops of 10 per cent KI and 10 grams of $NaHCO_3$, cool and titrate with iodine. The solution is made as directed on page 223.

The arsenic may be very satisfactorily determined as directed on page 157 by distillation, then dissolving the As_2S_3 and titrating as directed above.

Antimony.—The filtrate from the arsenic sulfide contains the antimony (and traces of tin). Evaporate nearly to dryness to remove the excess of acid, dilute to 25 c.c. and precipitate the antimony (and tin) with H_2S. Filter, dissolve with a little sodium sulfide (to remove traces of copper), filter again, make the filtrate acid and pass in H_2S. Filter on a weighed Gooch filter, wash with H_2S water, ignite and weigh as Sb_2O_4.

If the determination of tin is desired, it is separated from the antimony in the filtrate from the arsenic sulfide by Clark's oxalic acid method.

Bismuth.—The sulfide of bismuth left after the treatment of sulfides of arsenic and antimony with Na_2S is digested with 10 c.c. of nitric acid until dissolved, filtered, 1 c.c. of sulfuric acid added and evaporated to strong fumes to expel all nitric acid. Dilute to 50 c.c., add sulfurous acid and 10 c.c. of dilute KI solution, boil off any free iodine, filter if necessary and dilute to 100 c.c. in a graduated flask. According to the depth of color, take 10, 20 or 50 c.c. and transfer to a Nessler tube. Add a few cubic centimeters of dilute sulfurous acid. Into another tube put as much KI solution as in the assay tube, add sulfurous acid and then dilute to within a few cubic centimeters of the same bulk. Then add standard bismuth solution until the tints are the same. The color is due to the formation of bismuth iodide.

The standard bismuth solution is made as follows: Dissolve 0.1 gram of bismuth in a few drops of nitric acid, evaporate to fumes with 2 c.c. of sulfuric acid and dilute to 1 liter. The sulfurous acid used is made by diluting 10 c.c. of commercial acid to 1 liter.

One must be careful not to confuse the yellow color of free iodine with that of bismuth iodide. If the yellow color is removed by boiling and returns on standing, it is due to free iodine. Hence, the necessity of having a little sulfurous acid present to remove the iodine. But a strong solution of sulfurous acid will liberate iodine in the presence of H_2SO_4.

There should not be more than 1 mg. of bismuth in the tube or less than 0.1 mg. No elements interfere.

Selenium and Tellurium.—If these are wanted, they are precipitated before the arsenic, antimony and bismuth by passing SO_2 through the acid solution. This precipitates out the elementary selenium and tellurium. Filter them on a small Gooch mat, wash with water containing a little HCl and SO_2, dry at 104°C., weigh, ignite and weigh again.

Starch Indicator.—Starch prepared as follows is much more sensitive to iodine than when prepared in the ordinary way. When this indicator is used, it is more accurate to titrate arsenic than to weigh it.

Allow the raw wheat starch to stand for 24 hours in very dilute HCl, filter, wash and dry for three hours in an oven at 100°C. Boil 1 gram with 100 c.c. of water and filter.

Iodine Solution.—Dissolve 3.386 grams of pure iodine in 7 grams of KI and a little water and dilute to 1 liter. The end point in the titration is clearer if 3 drops of a 10 per cent solution of KI are added after the $NaHCO_3$ is added.

Lead, Iron, Nickel, Cobalt and Zinc.—Dissolve 50 grams of the copper in a mixture of 80 c.c. of sulfuric acid, 50 c.c. of nitric acid and 400 c.c. of water. Dilute to 600 c.c. and precipitate the copper on a large perforated platinum cylinder, using an 11×11-cm. cathode and a current of 3 amp. and preferably a rotating anode or a solenoid to rotate the solution. When the copper is all deposited, as shown by a test of a few cubic centimeters on a white plate with H_2S, evaporate the solution to a small volume, then transfer to a casserole and heat to fumes to remove the free sulfuric acid and most of the ammonium salts. The residue is dissolved in water and any lead sulfate and silica are filtered off. Hydrogen sulfide is then passed through the acidified filtrate and the precipitate filtered off and washed with hydrogen sulfide water. The precipitate is extracted with a little hot dilute sodium sulfide and the residue combined with the other precipitates containing lead, and the lead determined in them by electrolysis, including the lead originally deposited on the anode as peroxide.

The main solution (volume about 50 c.c.) is oxidized and the iron precipitated with NH_4OH. Aluminium, of course, also precipitates.

The filtrate is acidified with acetic acid and 1 c.c. of strong acetic acid is added in excess. Heat to boiling and pass hydrogen sulfide through. Filter off the ZnS, ignite and weigh as oxide. Make the filtrate alkaline with NH_4OH and precipitate the nickel and cobalt with H_2S, filter and ignite and weigh as oxides. Nickel and cobalt may be separated with dimethylglyoxime. (See page 123 *et seq.*)

DETERMINATION OF GASES IN COPPER

Pure CO_2 has no chemical action on red-hot copper. If copper drillings are heated red hot in a current of pure CO_2, the occluded gases are driven out and the loss in weight is the weight of these gases which were in the sample. If the sample is then heated in a stream of hydrogen, the combined oxygen in the copper is driven out in the form of water, but some hydrogen remains in the copper. This may then be driven out by igniting again in a stream of CO_2 and the loss in weight is oxygen and sulfur. The sulfur driven off is determined by passing the hydrogen, after it leaves the tube, into cadmium chloride solution and then titrating with iodine solution.

Process.—Produce CO_2 in a generator from pure sodium bicarbonate, or marble, and HCl. Purify the CO_2 by passing it through a train of the following reagents: (A) Saturated $KMnO_4$ solution. (B) Solution of silver sulfate. (C) Concentrated sulfuric acid. (D) A tube of dry chromous chloride. (E) Stick phosphorus. (F) Calcium chloride. (G) Phosphorus pentoxide. Also make pure hydrogen in a Kipp generator and purify the hydrogen by the following train: (A) KOH solution. (B) Strong sulfuric acid. (C) Palladiumized asbestos tube heated red hot. (D) Soda lime. (E) Calcium chloride. (F) Phosphorus pentoxide. The exit ends of the CO_2 train and the hydrogen train should be connected to a T-tube, to the other end of which is attached the ignition tube.

Put 50 grams of fine drillings in the ignition tube and weigh the tube and drillings. Attach the tube to the "T" and pass CO_2 through until all the air is driven out (about 30 minutes). Then heat the tube red hot for 30 minutes, while a rapid stream of CO_2 is passing. Cool the tube, without stopping the CO_2, and when cool displace the CO_2 with air by aspirating air through. Weigh. The loss in weight is occluded gases.

Again connect the ignition tube to the "T" and pass in hydrogen for 15 or more minutes, then keep at a red-heat for an hour or more, depending on the fineness of the drillings. The exit hydrogen must be passed through an ammoniacal $CdCl_2$ solution. After the hydrogen has been passed through long enough, shut it off and pass the CO_2 through the tube until the hydrogen is all displaced (at least 20 minutes). Cool the tube and, when cool, displace the CO_2 with air and weigh. The loss in weight is oxygen plus sulfur. Titrate the sulfur with iodine as directed on page 103. Subtract the weight of sulfur from the loss in weight to get the weight of oxygen in the sample.

Great care must be used to have the surface of the copper from which the drillings are taken perfectly clean and free from grease, etc.

The H_2O found may be caught in P_2O_5 and weighed. See determination of oxygen in steel, page 164.

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Am. Soc. Testing Materials, Standards, 1921.

Sulfur.—The only rapid and exact method which has appeared in print for the estimation of traces of sulfur in the refined product is the following, which depends upon the removal of the copper from its solution in pure nitric acid by electrolysis. The solution, freed from copper, is gradually transferred to a No. 3 *A* casserole and evaporated to dryness over an alcohol flame, with the addition of a little sodium carbonate to retain the sulfuric acid. The remaining nitric acid is removed by two evaporations with hydrochloric acid. A little HCl and 25 c.c. of water are added and the solution filtered. If any lead sulfate is found on the filters, they are boiled with a little sodium carbonate to render the sulfuric acid soluble, and filtered. The filtrates are combined and are then ready for precipitation by barium chloride. A blank analysis must be run with the acids and distilled water, which will usually show about 1 mg. of barium sulfate. When the copper contains much sulfur, it is necessary to use aqua regia for its solution, and to remove the hydrochloric acid by subsequent evaporations with nitric acid.

REFERENCE:

PRICE and MEAD, "Brass Analysis."

CHAPTER XXV

ANALYSIS OF REFINED LEAD

Process of Analysis.—Clean 100 grams of lead, and hammer or roll into thin plates, being very careful to use a perfectly clean and bright hammer and anvil to avoid introducing iron into the sample. Dissolve the lead in a large beaker on the hot plate in 100 c.c. nitric acid (sp. gr. 1.42) and 250 c.c. water. If the solution gets too hot, it will foam very much and run over, consequently it is necessary to watch it until most of the lead is dissolved. For the same reason, hammering or rolling the lead into very thin strips is not desirable.

After all the lead is dissolved, the solution is generally perfectly clear, although if more than 0.02 to 0.03 per cent of antimony or tin is present it will show some turbidity. Dilute the solution to nearly 500 c.c. to prevent lead nitrate from crystallizing out on cooling. If not perfectly clear, filter. Add 30 c.c. concentrated sulfuric acid previously diluted with water, and shake the flask. After settling, pour off the clear solution and wash the precipitate several times by decantation.

Evaporate the solution to fumes of H_2SO_4, take up with 50 c.c. of water and filter off the lead sulfate through the paper containing antimony and tin. Digest the lead sulfate with pure sodium sulfide solution, filter and add the other sodium sulfide solution obtained further on. Treat the filtrate from the lead sulfate, while hot, with H_2S for some time and pass the gas through until cold. After settling completely, filter, determine the iron and zinc in the filtrate, and treat the sulfides with Na_2S. Determine antimony and arsenic as described under copper analysis.

The insoluble sulfides of lead, bismuth, copper and silver may be dissolved in nitric acid, neutralized with sodium carbonate, and KCN added. Filter off lead and bismuth carbonates, acidify the filtrate with H_2SO_4 under the hood, filter off the AgCN and boil the solution to expel all HCN, after which determine the copper in the solution as follows:

Nearly neutralize the solution with NH_4OH, keeping the bulk small, say 50 c.c., add ammonium acetate, and divide into two equal parts. Add to one-half a fair excess of potassium ferrocyanide solution, and filter off the red precipitate immediately, passing through the paper twice if necessary. Add 1 c.c. acetic acid to each and the same amount of potassium ferrocyanide to the unfiltered half, and match the color in the filtered half by adding a weak copper sulfate solution of known strength from a burette, allowing one minute between each addition of copper sulfate for the color to develop.

The silver cyanide precipitate is not desired, for silver is determined by cupeling a separate sample of the lead.

To determine bismuth, dissolve the carbonates of lead and bismuth, in dilute nitric acid and precipitate as BiOCl, by Ledoux's method, thus: Nearly neutralize the nitric acid with NH_4OH, dilute to 300 c.c., complete the neutralization, add ⅓ c.c. HCl and heat nearly to boiling for an hour. Filter on a weighed Gooch crucible, wash with hot water, dry at 100°C. and weigh as BiOCl containing 0.8018 bismuth.

Notes on the Process.—To be sure of the results, it is necessary to run a check analysis on the nitric and sulfuric acids, evaporating the same amount of them nearly down to dryness, and treating the last of the sulfuric acid in the same way as the lead sample.

The results of refined lead analysis are apt to depend more upon the chemist than on the lead, and it is desirable that as many errors as possible be eliminated in order to get accurate results. One of the sources of error is in the chemicals used, which are not absolutely pure and import certain quantities of iron, copper, arsenic and antimony. The amount of nitric and sulfuric acids used is as great as the lead sample, so that a check should be run on the acids.

If bismuth alone is wanted, use the following method of Ledoux as given in Low's "Technical Methods of Ore Analysis," page 56.

Dissolve 25 grams of the lead in 200 c.c. of water and 40 c.c. of nitric of 1.42 sp. gr. Warm gently until all lead is dissolved, then add 1:2 NH_4OH, very cautiously, finally drop by drop until the free acid is gone and the liquid remains slightly opalescent. Now add 1 c.c. of 1:3 HCl. The solution will clear for a moment, then, if there is an appreciable amount of bismuth present, a crystalline precipitate of BiOCl will form. Heat nearly to boiling for an hour. Filter and wash the precipitate twice with boiling water. The precipitate will be contaminated with some lead and antimony. Dissolve it in a small amount of hot 1:3 HCl, wash the filter with hot water and dilute the filtrate with water, taking care that the dilution is not so great as to cause the precipitation of BiOCl. Pass H_2S through to precipitate the lead, bismuth and antimony as sulfides, filter, wash once with water, then with warm $(NH_4)_2S$ to dissolve the antimony sulfide, wash again with water and dissolve the bismuth and lead sulfides by placing filter and contents in a small beaker and heating with 1:4 nitric acid. Boil to disintegrate the paper and then filter and wash well with warm dilute nitric acid. Nearly neutralize the filtrate with NH_4OH, dilute to 300 c.c., complete the neutralization and add 1 c.c. of 1:3 hydrochloric acid. Keep hot for an hour, filter on a weighed Gooch crucible and wash with water, dry at 100°C. and weigh as BiOCl containing 80.18 per cent bismuth.

Bismuth may be determined in copper in the same way. The following is an analysis of refined lead in percentages:

Cu	Sb	Bi	Ag	Fe	Zn	Ni
0.0004	0.0008	0.002	0.0005	0.0006	0.0008	0.0007

REFERENCES:

BETTS, "Lead Refining by Electrolysis."
Am. Soc. Testing Materials, Standards, 1921.

Notes.—When separating the sulfides of arsenic, antimony and tin from sulfides of copper, lead, etc., it is necessary to wash all the sulfides back into the beaker in which they were precipitated. These sulfides sometimes cling so tenaciously to the paper that in dislodging them more water than the 25 c.c. specified is required. In this case allow the sulfides to settle and then decant the clear supernatant liquor through the filter until the volume is reduced to 25 c.c. Before rejecting the decanted fluid always test with H_2S water.

CHAPTER XXVI

THE ANALYSIS OF BEARING METALS

Bearing metals are alloys selected for bearing linings on account of their combination of antifrictional properties with sufficient compressive strength to prevent them from being squeezed out of place under high compression, and strength to avoid breaking under heavy shock.

They are usually composed of lead, tin, antimony and copper in about the following proportions: lead 70 per cent, tin 15 per cent, antimony 15 per cent, copper 0 to 6 per cent, when used for railroad trucks; but for automobile bearings the tin is high and the lead absent, the composition being about 84 per cent tin, 7 per cent copper and 9 per cent antimony. Journal brasses are composed of lead about 15 per cent, tin about 10 per cent and copper about 75 per cent.

There are many methods of analyzing alloys of lead, tin, antimony and copper, but the following method has given the writer the best results with a moderate expenditure of time.

When the alloy is digested with sulfuric acid under proper condition, the tin, antimony and copper all go in solution and the lead remains as insoluble lead sulfate. In the filtrate the antimony is found as $Sb_2(SO_4)_3$, the arsenic as $As_2(SO_4)_3$ and the tin and copper in their "ic" states. The arsenic is distilled off and titrated with iodine, antimony is titrated to the pentavalent state by standard permanganate and the copper precipitated as sulfocyanate after the antimony is titrated. Tin is determined in another sample in the filtrate from the lead sulfate, either with or without a previous titration of the antimony. The results obtained are excellent and the time and attention required slight. If copper is not wanted, lead, antimony and tin can be determined on the same sample.

Process of Analysis.—Place 1 gram of the fine drillings or shavings in a Kjeldahl flask, add 10 c.c. of sulfuric acid (sp. gr. 1.84) heat the flask over a bare flame and keep the sulfuric acid at or near boiling until the residue in the flask is pure white. Cool, add 20 c.c. of water all at once to the sulfuric acid, boil for several minutes, allow the lead sulfate to settle a few minutes, cool to about 50°C. and pour the clear liquid through a weighed Gooch crucible with an asbestos mat, without allowing the lead sulfate to pass out of the flask. Put 10 c.c. more strong sulfuric acid in the flask and heat at boiling temperature for 15 minutes, cool, add 30 c.c. of water, boil, cool and filter through the same Gooch as before. Wash all the lead sulfate out of the flask into the Gooch crucible, wash the crucible and sulfate five times with small amounts of water, and carefully ignite the crucible. To do this place the crucible inside a large one and heat the outside one to a dull red for 10 minutes, or, better, heat in a dull red-hot muffle. Cool and weigh. The weight of the lead sulfate multiplied by 0.683 gives the weight of the lead.

If arsenic is present, proceed as directed on page 197; if not, proceed as directed below.

Antimony.—To the filtrate, which should be less than 150 c.c. in volume, add 5 c.c. of HCl, cool to 15°C. and titrate with standard permanganate solution. Run in the permanganate until the pink color persists 30 seconds. The $KMnO_4$ should be standardized against pure antimony treated in the same way. The iron value of the permanganate multiplied by 1.076 theoretically equals the antimony present. That is, a permanganate solution, 1 c.c. of which equals 0.010 gram of iron, equals 0.01076 gram, theoretically, of antimony. The end point is sharp and the results exact.

Copper.—Now add 3 grams of tartaric acid to the solution and then NH_4OH until the solution is slightly alkaline, then add 2 c.c. of sulfuric acid and heat almost to boiling. Add 2 grams of Na_2SO_3 and when all is dissolved add a gram of KCNS dissolved in 10 c.c. of water. Shake the flask well and allow the precipitate to settle for 15 minutes while the solution is kept hot. Filter through an asbestos mat, wash well with water and then pour through the filter 40 c.c. of 10 per cent NaOH, catching the solution in a clean beaker or flask. Wash the filter well with water and titrate the sulfocyanate as directed on page 241, for the analysis of copper ores, or, better, dry the CuCNS to constant weight at 105°C., and weigh.

Tin.—At the same time that the above analyses are being made, carry through another sample up to or through the titration for antimony, thus getting checks on the lead and antimony results. Then add to the solution one-third its volume of strong HCl, transfer the solution to a 500-c.c. flask and stopper the flask with a three-hole stopper. Through one hole pass a glass tube which extends to the bottom of the flask. Through another pass an iron rod, the end in the flask being bent into a coil.

Add to the solution 5 c.c. of sulfuric acid containing 0.15 gram of antimony unless the sample contains a sufficient amount already. Heat to boiling and pass a stream of CO_2 or natural gas, freed from H_2S by NaOH, through the solution by means of the glass tube. Continue the boiling (and current of gas) for 20 minutes after the solution becomes colorless. Cool the solution under a jet of water without stopping the current of gas, which should pass through rapidly while the flask is cooling to prevent the air from being drawn in. When cool, run in through the vacant hole 100 c.c. of distilled water, 3 c.c. of starch solution, draw up the iron rod, and titrate the tin with a N/10 solution of iodine. The blue end point fades after about a minute.

MODIFICATION WHEN ARSENIC IS PRESENT

If the metal contains arsenic, the above process must be modified because arsenic interferes with the determination of antimony.

Process of Analysis.—Evaporate the filtrate from the lead sulfate until fumes of sulfuric acid appear, cool, add 15 c.c. of water, 35 c.c. of HCl (sp. gr. 1.20) and insert in the flask a clean rubber stopper, carrying a centigrade thermometer and a delivery tube. The thermometer should be about 1 in. from the surface of the liquid, so as to get the vapor temperature only, which should not go above 108°C. Connect the delivery tube to a figure-S condenser, which has one of its curves nearly filled with water and submerged in cold water in a 500-c.c. beaker, and its other free end dipping into about 75 c.c. of 1:1 HCl in a 300-c.c. flask, through which a slow stream of H_2S is passing.

The S-condenser is about 18 in. long and ½ in. inside diameter, but tapers to about ¼ in. at the upper and ⅛ in. at the lower end to facilitate washing and to make the bubbles of gas small as they emerge into the beaker. This makes a perfect condensing apparatus in this case; it is very simple, easy to handle, has only one rubber connection besides the rubber stopper, and no cocks or corks that leak. Nothing is lost through it except air from the flask at the very start.

Distill from 10 to 15 minutes, boiling gently, and keeping the vapor temperature at 107° for at least five minutes. The arsenic, as $AsCl_3$, is all distilled over, even if the alloy contains 5 per cent, which is rare.

Arsenic.—The $AsCl_3$ obtained above is impure from antimony. If necessary, add more HCl to make a solution of 1.10 sp. gr., warm somewhat and pass H_2S through the solution until all the As_2S_3 is precipitated. Filter through a small amount of macerated filter paper compressed into the tip of the funnel, wash several times with 1:1 HCl, then with water, dissolve in the smallest possible amount of $(NH_4)_2S$, catching the filtrate in a Kjeldahl flask. Add 1 gram of potassium sulfate and 5 c.c. of strong H_2SO_4 and heat until the H_2SO_4 has fumed strongly for several minutes, cool, add a few crystals of tartaric acid and fume until colorless. Cool, dilute, neutralize and titrate as directed on page 223.

Antimony.—Cool the solution left in the flask, add about 150 c.c. of cold water and the filtrate from the As_2S, from which all H_2S has been expelled by boiling, and titrate with standard permanganate solution. The blank is 0.1 c.c. About 4 c.c. of hydrochloric acid should be present during this titration; usually enough is left in the flask from the distillation. The solution must be cold when titrated.

Tin.—Determine the tin as directed above.

Notes on the Process.—Arsenic consumes close to 1.5 times as much permanganate solution as antimony does. Hence, if the arsenic is not removed before the antimony determination, the results will be worthless. Most all alloys which contain antimony contain arsenic. The arsenic should be removed before the tin determination, since it often causes high results in this case too.

Copper has no effect whatever on the antimony determination, but when it exceeds about 3 per cent it is apt to interfere with the tin determination. The amount of iron found in alloys is usually entirely oxidized in the concentrated sulfuric acid to the ferric state, so that it does not interfere. There are no other common metals that interfere.

About the only causes of error in this method are too great a variation from the conditions stated and the use of impure chemicals.

For the reactions and remarks for the copper titration, see page 241. For those for the tin titration, see page 216. For the arsenic titration, see page 223.

When the alloy containing antimony is dissolved in strong hot sulfuric acid, the antimony goes into solution as $Sb_2(SO_4)_3$. This is titrated by the permanganate, thus:

$$5Sb_2(SO_4)_3 + 4KMnO_4 + 24H_2O = 10H_3SbO_4 + 2K_2SO_4 + 4MnSO_4 + 9H_2SO_4.$$

When the antimony is being titrated without HCl the solution will become pink long before the end point is reached; in fact, the pink appears soon after the titration is started. The permanganate must be added until the solution becomes a deep permanganate color and the excess is then titrated with ferrous sulfate. If the solution contains 20 per cent HCl, the pink color does not appear before the end point is reached, but the end color is evanescent. About 5 c.c. in 150 c.c. is correct.

REFERENCES:

DEMOREST, *J. Ind. Eng. Chem.*, **5**, 842.
STIEF, *J. Ind. Eng. Chem.*, **7**, 211.

REFERENCES ON OTHER METHODS:

LOW, "Technical Methods of Ore Analysis," p. 333
PRICE and MEAD, "Technical Methods of Brass Analysis," pp. 157, 164.
MCCAY, *J. Am. Chem. Soc.*, **31**, 373 (separation of Sn and Sb).
DINAM, *Mon. Sci.*, **22**, 600.
KIETREIBER, *Oesterr. Chem. Ztg.*, **13**, 146.
GOODWIN, *J. Ind. Eng. Chem.*, **3**, 34.
KOPENHAGUE, *Ann. chim. Anal.*, **17**, 241.
MCCAY, *J. Am. Chem. Soc.*, **32**, 1241.
Am. Soc. Testing Materials, Standards, 1921.

CHAPTER XXVII

BRONZE AND BRASS ANALYSIS

Brass is essentially an alloy of copper and zinc and bronze an alloy of copper and tin, but brass may have small amounts of lead, tin and other elements, and bronze may have small amounts of lead, zinc and other elements.

Analysis of Brass.—Dissolve 1 gram of the drillngs with a mixture of 5 c.c. of water and 10 c.c. of nitric acid. Cover with a glass and heat nearly to boiling and, when the solution is complete, evaporate to dryness, but do not bake the residue. Moisten the residue with 5 c.c. of strong HNO_3 and digest for 10 minutes. Add 50 c.c. of hot water and digest for one hour, if there is any residue. Filter through a paper on which has been sucked macerated filter paper by means of a suction filter arrangement. Wash well and, if accurate results are not desired, ignite the precipitate in a porcelain crucible and weigh as SnO_2 containing 78.8 per cent tin. Since the SnO_2 is contaminated with all the phosphorus in the sample and with iron and more or less copper and lead, if present, it must be purified if accurate results are required. To do this, peel the mat of macerated paper and the precipitate of metastannic acid off of the filter paper, put it in the beaker in which the sample was dissolved and add 10 c.c. of NH_4HS made by saturating ammonia with H_2S. Heat until all the precipitate is dissolved except the small amount of sulfides of copper and lead, etc. Filter through the same paper as before and wash well with dilute NH_4HS water. Dissolve the sulfides on the paper in a small amount of 1:1 HNO_3 and bromine water, boil off the bromine and add the solution to the main solution of the copper. Keep the ammonium sulfide solution of tin for the determination of tin.

Copper and Lead.—Add water sufficient to bring the volume to 150 c.c., add 15 c.c. of HNO_3 and electrolyze, using gauze anode and cathode. Use a current of about 0.5 amp. only until the lead is precipitated as PbO_2 on the anode, then increase the current strength to 2 to 4 amp. and continue electrolysis after a sufficient amount of ammonia has been added to leave only 5 per cent of HNO_3 present; finish the electrolysis as directed on page 236.

If the brass contains manganese, the PbO_2 will be contaminated with it. Dissolve the PbO_2 in 1:3 HNO_3, with the addition of a few crystals of KNO_2, and determine the manganese by the bismuthate process. Calculate the manganese to MnO_2 and subtract from the weight of the impure PbO_2.

Zinc and Iron.—After the lead and copper are deposited by the electrolysis method as above directed, add 10 c.c. of HNO_3, then neutralize with ammonia and add a slight excess. Boil, filter off the $Fe(OH)_3$ and wash twice, redissolve in 10 c.c. of 1:1 HNO_3 and again precipitate and filter and wash the $Fe(OH)_3$ thoroughly. Determine the iron as directed on page 380.

Nickel and Zinc.—The filtrate contains the zinc, nickel and part of the manganese in the original sample. Divide into two equal parts and in one determine the nickel by the dimethylglyoxime method as directed on page 123. Add HNO_3 to the other half until slightly acid, then add 3 c.c. more and titrate with ferrocyanide solution as directed on page 204. The filtrate from the dimethylglyoxime precipitate may also be used for determination of zinc. The zinc may also be precipitated as phosphate as directed on page 207.

Tin.—The solution of tin in ammonium polysulfide obtained above contains all the tin. Heat to boiling until a precipitate starts to form, add 10 c.c. of HNO_3 and evaporate to dryness. Add dilute HNO_3, heat to boiling, filter and wash the metastannic acid. Ignite very slowly and, finally, strongly, cool and weigh as SnO_2. Multiply by 0.7881 for the weight of the tin.

Instead of determining the tin gravimetrically, add 50 c.c. of 1:2 HCl and determine as directed on page 197.

Notes.—The method as above given can be greatly shortened for the analysis of brasses practically free from tin.

Metastannic acid when precipitated from HNO_3 solution is practically complete unless large amounts of iron are present, if the HNO_3 solution is not allowed to become cold before the precipitate is filtered. If it cools, some metastannic acid goes back into solution.

Manganese may be accurately determined by the chlorate method as given on page 76.

REFERENCES:

HEATH, "Analysis of Copper."
IBBOTSON and AITCHISON, "The Analysis of Non-ferrous Alloys."
PRICE and MEADE, "Technical Analysis of Brass."
HALL and WILLIAMS, "The Examination of Iron, Steel and Brass."
Am. Soc. Testing Materials, Standards.

The Analysis of German Silver.—This is an alloy of copper, nickel and zinc, with small amounts of other metals.

Procedure.—Dissolve ½ gram of the drillings in nitric acid, evaporate just to dryness, add 100 c.c. of 1:20 HNO_3, digest and filter off any metastannic acid, wash, ignite and weigh. Electrolyze the filtrate to determine the copper and lead. Then add ammonia until barely alkaline, heat to boiling and filter off the ferric hydroxide, wash, ignite and weigh. Add 5 c.c. of H_2SO_4, evaporate to fumes, cool and dilute to 150 c.c., add ammonia until barely alkaline and precipitate with dimethylglyoxime, using four times as much glyoxime by weight as the weight of the nickel. Heat near to boiling for half an hour, filter the nickel dimethylglyoxime and wash at least 15 times. Dry at 105°C. and weigh (see page 123). In the filtrate determine the zinc by precipitating as zinc ammonium phosphate, as directed on page 207. In high nickel alloys, as monel metal and nichrome, the above process is not satisfactory, owing to the extremely large precipitate of nickel dimethylglyoxime. In these alloys it is best to precipitate the nickel as sulfide from an alkaline solution, wash and ignite, dissolve the nickel oxide in HNO_3, evaporate with H_2SO_4 and weigh as $NiSO_4$.

CHAPTER XXVIII

THE DETERMINATION OF ZINC IN ORES

Zinc usually occurs in ores as sulfide, oxide, carbonate or hydrosilicate. All of these minerals are decomposed by boiling in the proper mineral acids. Ores containing zinc spinel (gahnite) cannot be decomposed by acids and must be fused before treatment with acids. Oxidized ores should be first treated with HCl before nitric acid is used.

Solutions of zinc in hydrochloric acid are completely precipitated by potassium ferrocyanide. Many other metals are also precipitated by this reagent, including iron, copper, manganese and cadmium, and if these are present in the ore, they must be removed before the zinc is titrated.

The hydrochloric acid solution of zinc which is to be titrated must not contain free chlorine, bromine or oxides of chlorine, as these decompose the ferrocyanide and produce a green-colored precipitate, making results run high. Zinc ferrocyanide is white. The following method is the process of von Schulz and Low modified.

Process of Analysis.—Place 1 gram of the ore in a 250-c.c. casserole, add 5 c.c. of HCl and 10 c.c. of HNO_3 and evaporate nearly to dryness, then cautiously add 25 c.c. of HNO_3, previously saturated with $KClO_3$ by shaking up with crystals of the salt. (Keep this solution in an open bottle.) When the violent action is over, cover the casserole and boil rapidly to dryness. Do not bake the residue. Now cool and add 7 grams of NH_4Cl, 25 c.c. of hot water and 15 c.c. of strong NH_4OH. Boil the liquid one minute, add bromine water and then rub the dish with a rubber-tipped rod to loosen and disintegrate all the insoluble matter. Filter and wash several times with a boiling-hot 1 per cent solution of NH_4Cl. If the filtrate is *blue*, copper is present.

If the residue is large in amount, dissolve it in 10 c.c. of 1:1 HCl, add ammonia until alkaline and 2 grams of ammonium persulfate and some bromine water to precipitate manganese, heat to boiling, filter and add the filtrate to the previous one. Wash with a hot 1 per cent NH_4Cl solution.

Make the filtrate, which should amount to about 200 c.c. acid with HCl, keeping the cover on to prevent loss due to effervescence. Then add 20 c.c. more of HCl (sp. gr. 1.2) heat to 70°, pass H_2S through the solution for several minutes and when the copper is practically all precipitated, gradually and with stirring, add 10 c.c. of NH_4OH (sp. gr. 0.9) and continue to pass the H_2S for several minutes. Again heat to 70°C. and titrate with ferrocyanide. The volume at the beginning of the titration should be about 250 c.c. Of this 50 c.c. may be reserved until the other four-fifths is titrated, then the 50 c.c. is added and, knowing the approximate end point, the titration can be finished without consuming much time. The titration must be performed slowly and with constant stirring to get the best results. Electrometric titration makes an indicator unnecessary. See page 255.

Standardization of the Ferrocyanide.—Dissolve 22 grams of pure $K_4Fe(CN)_6 \cdot 3H_2O$ in water and dilute to 1 liter. One cubic centimeter of this solution will precipitate approximately 0.005 gram of zinc.

Weigh 0.2 gram of pure zinc, or, better, the amount of zinc which is approximately that which the sample is supposed to contain. Dissolve in 10 c.c. of HCl and 20 c.c. of H_2O, add 10 grams of NH_4Cl, dilute to 250 c.c., heat to 70°C. and titrate. Run in the ferrocyanide slowly and with constant stirring until a drop of the solution shows a brown tinge when tested on a white plate with a drop of a 5 per cent solution of uranyl nitrate after standing a minute.

A blank must be run, using the same amount of reagents and solution as in the standardization. This generally takes about 0.3 c.c. of the above solution and this amount must be subtracted from the amount of ferrocyanide used in the standardization and in the titration of the ore. It is necessary that standardization be made under the same conditions of temperature, volume and acidity as obtain when the ore is titrated.

Notes on the Process.—Manganese is precipitated at the first from the acid solution as MnO_2 by means of potassium chlorate, because when it is precipitated from an alkaline solution as MnO_2 it carries down zinc as zinc manganite.

When the copper is precipitated according to the above directions, that is, by hydrogen sulfide from a very acid solution, the copper comes down free from zinc. What little copper remains in solution is precipitated as the solution is gradually made less acid. The copper sulfide need not be filtered off, as it does not interfere with the titration, even when the copper is present in amounts as high as 20 per cent of the sample, for it precipitates in a very dense form.

The potassium chlorate used in the decomposition of the ore introduces no complications unless used in abnormally large amounts, for it is reduced by the action of the hydrogen sulfide and the presence of the hydrogen sulfide during titration prevents any oxidation of the ferrocyanide.

The use of lead or aluminium to precipitate the copper and cadmium is inadvisable, as they tend to make results erratic. Lead is least harmful.

The titration for standardization should be made under the same conditions as to temperature, acidity, volume, amount of ammonium salt and rate of titration as obtains when the ore is titrated. The amount of free acid should not be greater than about 5 per cent of HCl (sp. gr. 1.2).

It is absolutely necessary that the titration should not be made too rapidly. If the ferrocyanide be run in rapidly and without much stirring, the end point will seem to be reached long before the zinc is all precipitated. If, however, the solution be then allowed to stand for several minutes while being vigorously stirred, the titration may be finished without error. Probably, when the ferrocyanide is added rapidly zinc potassium ferrocyanide is precipitated, which can react with uranyl nitrate, giving a brown color.

If zinc spinel is in the ore, the method must be modified as follows: The ore is dissolved as above. The gangue left on the filter paper should be ignited and fused with sodium carbonate mixed with a little borax glass, until decomposition is complete. The melt is dissolved in HCl and added to the main solution, and the analysis carried on as usual.

None of the constituents of zinc ores except cadmium interferes with the above process. Nickel, if present, would count as zinc. The writer has tested the method on the Government standard ore, which contains 31.4 per cent zinc. He put in 10 per cent each of manganese, iron, copper and lead without causing more than $\frac{1}{10}$ to $\frac{2}{10}$ per cent error.

REFERENCES:

Low, "Technical Methods of Ore Analysis."
DEMOREST, *J. Am. Chem. Soc.*, **5**, 302.
J. Am. Chem. Soc., **4**, 468 (complete bibliography).

Sulfide Separation of Zinc.—The exact determination of zinc by the following process is considerably longer than the method of Low but yields very dependable results. It depends upon the precipitation of zinc with H_2S in a solution less than N/10 acid with H_2SO_4. It has been shown by Weiss that the precipitation of ZnS from this dilute H_2SO_4 solution is quite complete, but it is not complete from HCl solutions of similar strength. Weiss has also shown that a rapid stream of H_2S must be used, a slow current causing incomplete precipitation. The method as here written is largely as given by Scott.

Process of Analysis.—Weigh an amount of the finely ground ore sufficient to contain approximately 0.40 grams of zinc. Transfer to a 200-c.c. beaker, add 10 c.c. of water and 15 c.c. of HCl (sp. gr. 1.20). Cover with watch-glass, heat and after a few minutes add 5 c.c. of HNO_3. Heat until the solution of all sulfides is complete, adding more HNO_3 if necessary. Add 10 c.c. of 1:1 H_2SO_4, break up any cake which may have been formed on the bottom of the beaker with a stirring rod and evaporate until copious fumes of SO_3 appear. Cool, dilute to 50 c.c. and add 1 gram of granulated aluminum, cover with a watch-glass and heat for about 15 minutes. This will reduce all the H_2S metals (Cd only partially) and all the iron to ferrous iron. Filter off the silica and precipitated metals and wash with hot water. Add 5 c.c. of 1:1 H_2SO_4, dilute to 100 c.c. and pass a rapid stream of H_2S through the *cold* solution for 15 minutes. Drop in 1:4 ammonia carefully until yellow CdS precipitates. Heat the solution to 80°C. and continue to pass H_2S for a few minutes. Filter through a filter paper with a mat of macerated filter paper sucked tightly on it. Wash the precipitate with cold 8 per cent H_2SO_4 several times, then with hot water until all zinc is removed.

Heat the filtrate to boiling to remove all H_2S, cool, add dilute KOH solution until nearly neutral, then dilute K_2CO_3 until methyl orange becomes neutral but not alkaline. Dilute to 200 c.c. and add 4 c.c. of 5 per cent H_2SO_4. *Cool* to tap-water temperature, and pass a *rapid* stream of H_2S through the solution for three-quarters of an hour. Allow the precipitate to settle 10 or 15 minutes, filter and wash with cold water. A hole is punched in the filter paper and the sulfide washed back into the beaker in which it was precipitated. The filter paper and glass tube are then washed with 10 c.c. of HCl in hot water, catching the washings in the same beaker. Boil off the hydrogen sulfide, add 13 c.c. of ammonia (sp. gr. 0.9), neutralize with HCl, add 3 c.c. excess and dilute to 200 c.c. Heat to boiling and titrate as under "Standardization." When Cd is absent or present in quantities less than 0.05, the procedure is, of course, shortened considerably. The electrometric titration makes unnecessary the use of an indicator (see page 255).

If the end point should be passed, add a measured amount of standard N/10 $ZnCl_2$ solution and finish the titration, making proper correction.

Standardization of Ferrocyanide.—Weigh 0.4000 gram of purest zinc, put in an Ehrlenmeyer flask and dissolve in 10 c.c. of HCl (sp. gr. 1.2). When dissolved, add 50 c.c. of water and 13 c.c. of ammonia (sp. gr. 0.9) and then HCl until acid and 3 c.c. in excess. Add 0.0004 gram of ferrous iron (1 drop of N/10 ferrous sulfate), dilute to 200 c.c. heat to boiling and titrate with ferrocyanide made as directed on page 204, or as follows.

Reserve one-fourth of the solution. Add the ferocyanide to the hot solution slowly and with stirring until the bluish color changes to a creamy white. Pour in all but 10 c.c. of the reserve solution and titrate as before and add ½ c.c. excess. Wash all the remainder of the zinc solution into the flask and finish the titration drop by drop until the blue color fades sharply to a green. Duplicate standardizations must, of course, be made. It is necessary to add the slight excess of ferrocyanide near the end to be sure of a precipitate of normal composition.

REFERENCES:

STONE and WARING, *J. Am. Chem. Soc.*, **29**, 262.
SCOTT, "Standard Methods of Chemical Analysis."

To determine the zinc as pyrophosphate, filter the solution of the ZnS in hydrochloric acid and make the filtrate cold, dilute and slightly acid. Then add a *large* excess of ammonium sodium hydrogen phosphate and neutralize very carefully with NH_4OH, adding it drop by drop, finally adding a drop or two in excess. Finally, add about 1 c.c. of acetic acid and warm gently until the flocculent precipitate of $ZnNH_4PO_4.H_2O$ has settled as a dense crystalline powder. Filter and wash with hot water.

Dry the precipitate, separate the paper from it and burn the paper. Add the ash to the precipitate and ignite the two, gently at first, then for a few minutes at a bright red-heat. Cool and weigh as $Zn_2P_2O_7$, containing 42.89 per cent of zinc.

Notes on the Process.—The flocculent $ZnNH_4PO_4.H_2O$ is very soluble in the mineral acids as well as in ammonia, but after crystallization it is much less soluble in the latter. It is only slightly soluble in acetic acid; an excess of 1 c.c. in 100 c.c. of solution does not dissolve an appreciable amount. It is somewhat soluble in all ammonium salts unless considerable excess of phosphate is present.

Instead of weighing the zinc as pyrophosphate, the zinc sulfide may be dissolved in H_2SO_4 evaporated and weighed as zinc sulfate as directed for manganese on page 8. This is quite accurate.

CHAPTER XXIX

THE DETERMINATION OF LEAD IN ORES

Lead occurs in ores chiefly as the minerals galena (PbS), cerrusite ($PbCO_3$) and anglesite ($PbSO_4$). It also occurs as molybdate, phosphate and arsenate.

Lead ores are completely soluble in acids, hence require no fusion.

Lead is determined satisfactorily either by gravimetric or volumetric methods. The gravimetric methods depend upon the precipitation of lead as lead sulfate or electrolytically as PbO_2. Volumetric methods depend upon the precipitation of lead as lead molybdate or lead chromate.

THE ELECTROLYTIC DETERMINATION OF LEAD

Lead is precipitated on the anode from a nitric acid solution as PbO_2. The precipitation is rapid, owing to the high atomic weight of lead and the small solution tension of PbO_2 in nitric acid. The precipitated PbO_2 does not adhere well to a smooth, flat electrode, but adheres well to a gauze electrode, so well, in fact, that it cannot be rubbed off with the finger.

If bismuth or antimony are present, they will partially deposit with the lead, and manganese will also deposit as MnO_2 with the lead unless the solution is very acid. The presence of arsenic, selenium or tellurium will prevent the precipitation of the PbO_2 partially or wholly. If any of these are present they must be removed by chemical means, which is easily done. Phosphoric acid, if present, will prevent the precipitation of lead.

Process of Analysis for Ores Free from Arsenic, Antimony or Bismuth.—Weigh an amount of sample containing not more than 0.5 gram of lead. Put it in a 250-c.c. beaker, add 10 c.c. of strong HCl and heat to boiling for several minutes. Then, when most of the sulphur is driven off as H_2S, add 15 c.c. of HNO_3 and continue the heating until the ore is all decomposed and finally boil vigorously to expel all chlorine. There must be no chlorine present during the electrolysis. Add 20 c.c. of water and then

NH_4OH until there is considerable excess and heat until any lead sulfate is dissolved. Then add HNO_3 until there is 15 c.c. excess present, dilute to 100 c.c. and electrolyze, using a gauze anode. With a cylindrical gauze anode ¾ in. in diameter and 2½ in. high a current of 3 amp. and a potential of about 3 volts will cause complete deposition in 15 minutes to a half hour. It is best to electrolyze in a hot solution.

Break the current and set the anode in a beaker of pure water, then remove and dry at a temperature of 230° in an oven. Cool and weigh. Multiply the PbO_2 by 0.8640 to get the weight of the lead.

To remove the PbO_2, set the electrode in a beaker containing warm 1:3 HNO_3 and add a few cubic centimeters of alcohol or formic acid. The PbO_2 is reduced to PbO, which is soluble in nitric acid.

If the ore is soluble in nitric acid, the HCl may be dispensed with and the sample treated directly with the nitric acid. This will cause the formation of considerable lead sulfate, which will dissolve when the solution is made alkaline and heated.

Method of Ores Containing Antimony or Bismuth.—Dissolve the ore as above directed and then add 50 c.c. of 10 per cent H_2SO_4 which has been saturated with lead sulfate by adding a few drops of lead acetate, shaking well and allowing to stand until lead sulfate settles clear. Evaporate to very copious fumes of H_2SO_4. Cool and add 30 c.c. of water containing 3 grams of tartaric acid to keep the antimony in solution. Heat to boiling to dissolve all soluble salts, cool, filter and wash three times with cold water. Wash the lead sulfate back into the beaker with a small amount of water and pour through the filter into the beaker hot ammonium nitrate solution, made by adding to 30 c.c. of 1:1 nitric acid 10 c.c. NH_4OH. This will dissolve any lead sulfate left on the paper. Digest the solution in the beaker until the lead sulfate is all dissolved, then add nitric acid until there is 15 c.c. excess present, heat and electrolyze as above.

To test the purity of the deposit the following method is good: Place the anode in a beaker containing 40 c.c. of 1:3 nitric acid, add a few cubic centimeters of formic acid and heat until all PbO_2 is dissolved. Wash the anode, catching the washings in the beaker, add 5 c.c. of sulfuric acid and evaporate to copious fumes.

Cool, add 30 c.c. of water and heat to boiling several minutes to change any lead bisulfate to sulfate. Cool, add 5 c.c. of alcohol, allow to settle and filter in a weighed Gooch crucible and wash several times with 10 per cent alcohol. Ignite for five minutes at a barely visible red over a Bunsen burner. Weigh and multiply the weight of lead sulfate by 0.6830. Ores may also be analyzed in this way if the analyst prefers to weigh lead sulfate instead of PbO_2. That is, the ore is dissolved as in the method for ores free from bismuth and electrolyzed. Then the PbO_2 (with oxides of bismuth and antimony and manganese, possibly) is dissolved with nitric and formic acids and evaporated to copious fumes. Then 30 c.c. of water are added and boiled, cooled, filtered and the lead sulfate washed with 10 per cent alcohol. The Gooch crucible and the precipitate are heated for five minutes over a Bunsen burner, cooled and weighed. No elements interfere and very good results are obtained.

Permanganate Method.—The PbO_2 obtained by electrolysis may be impure from the presence of arsenic, antimony or manganese. The error due to the presence of arsenic and antimony, which may have precipitated because of using the direct method of electrolysis without previous removal of arsenic and antimony, may be corrected as follows: Put the anode with the deposited PbO_2 in a tall beaker, cover with water and add 5 c.c. of HNO_3 free from nitrous acid, add standard H_2O_2 solution until the PbO_2 is completely dissolved. Now titrate the excess H_2O_2 promptly with standard permanganate. Add the same amount of H_2O_2 solution as used and titrate again with permanganate. The difference between the amounts of permanganate used in the two titrations gives the permanganate equivalent to PbO_2.

The H_2O_2 solution is made by dissolving 20 c.c. of U.S.P. H_2O_2 in a liter of water and adding 50 c.c. of HNO_3. The reactions are:

$$PbO_2 + H_2O_2 + 2HNO_3 = Pb(NO_3)_2 + 2H_2O + O_2.$$

$$5H_2O_2 + 2KMnO_4 + 6HNO_3 = 2KNO_3 + 2Mn(NO_3)_2 + 8H_2O + 5O_2.$$

Hence $2KMnO_4 = 5Pb = 10Fe$ and, theoretically, $\frac{5Pb}{10Fe} = 1.851$, but actually the ratio is found to be 1.92.

REFERENCES:

- SMITH, "Electroanalysis."
- PERKIN, "Practical Methods of Electrochemistry."
- BENNER and ROSS, "Electrolytic Determination of Lead in Ores," *Mining Sci. Press*, **101,** 642.
- LIST, *Metal. Chem. Eng.*, **10,** 135.
- BENNER, *J. Ind. Eng. Chem.*, **2,** 348.
- WOICIECHOWSKI, *Met. Chem. Eng.*, **10,** 108.

For the determination of lead by the molybdate method of Alexander, see Low, "Technical Methods of Ore Analysis." This method is less reliable, and no more rapid, than the dichromate method, and so is not given here.

For the permanganate method for lead, see BOLLENBACH, *Chem. Ztg.*, **33,** 1142.

THE VOLUMETRIC CHROMATE METHOD FOR LEAD

The following method is the one devised by Guess and modified by Low and Waddell. Low says, "I find it more generally satisfactory than any other."

It depends upon the precipitation of lead chromate from an acetic acid solution which is then dissolved in hydrochloric acid, potassium iodide added and the liberated iodine titrated with standard thiosulfate solution.

Solutions Required. Extraction Solution.—Make a cold saturated solution of sodium acetate and filter it. Dilute it with two volumes of water and add 30 c.c. of 80 per cent acetic acid per litre.

Hydrochloric Acid Mixture.—Make a cold saturated solution of NaCl and filter it. To 1 liter of the salt solution add 250 c.c. of water and 100 c.c. of hydrochloric acid (sp. gr. 1.2).

Potassium Dichromate.—Make a cold saturated solution of the commercial salt and filter it.

Starch Solution.—Make as directed on page 97.

Process of Analysis.—Weigh 0.5 gram of the ore and put it into a 150-c.c. flask. Add 10c.c. of strong HCl and heat until no more H_2S comes off. Add 5 c.c. of nitric acid and boil until the ore is completely decomposed. Now add 10 c.c. of 1:1 sulfuric acid and boil until copious white fumes come off. Cool, add 50 c.c. of water and heat to boiling until all the soluble salts are dissolved, cool and add 5 c.c. of ethyl alcohol, allow to settle, then filter through a 9-cm. filter and wash with cold 10 per cent sulfuric acid solution five times and then twice with water.

Have the extraction solution nearly boiling, and with a fine jet wash the lead sulfate back into the flask, then wash the filter thoroughly with the hot solution until all lead sulfate remaining on it is dissolved, catching the washings in the flask containing the rest of the lead sulfate, and taking care to wash under the folds of the filter paper. Heat the filtrate to boiling and add more of the acetate solution if necessary to dissolve all of the lead sulfate. Finally, dilute to 150 c.c., heat to boiling, add 10 c.c. of the dichromate solution and boil for seven minutes. It is necessary to boil about this length of time to insure always the same constitution of the lead chromate. Now filter through a large filter paper and wash the flask and precipitate 10 times, with a hot solution of sodium acetate made by diluting 50 c.c. of a cold saturated solution to 1 liter. Place the clean flask under the funnel, and with a jet of the cold HCl mixture dissolve the precipitate on the filter. Continue the washing and stirring up of the precipitate with the HCl mixture until all the residue and all color are removed from the filter. Use at least 50 c.c. of the mixture.

Now add 4 c.c. of a 25 per cent solution of KI and titrate at once with standard sodium thiosulfate solution. Continue adding the thiosulfate until the brown color of the liberated iodine becomes faint; then add enough starch solution to produce a strong blue color and continue the titration until the solution becomes a pale green with no tinge of blue. The end point is very sharp.

Standardize the thiosulfate solution on pure lead. The reactions in the determination are:

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2.$$

$$2H_2CrO_4 + 6KI + 12HCl = 6KCl + 2CrCl_3 + 8H_2O + 6I.$$

$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$

Therefore, 1Pb equals $1H_2CrO_4$, which liberates 3I, which equals $1Na_2S_2O_3$. That is, to titrate the iodine liberated by the H_2CrO_4 from 1Pb requires $3Na_2S_2O_3 \cdot 5H_2O$. Then to make a solution of thiosulfate, 1 c.c. of which will equal 0.005 gram of lead, will require, for 1 liter, the amount of thiosulfate indicated by the following proportion: $Pb:3Na_2S_2O_3 \cdot 5H_2O::x:5$, or 17.985 grams per liter. The thiosulfate solution used for the copper determination will do. To standardize, dissolve about 0.2 gram of pure lead in 15 c.c. of 1:2 nitric acid, add 5 c.c. of sulfuric acid and evaporate to strong H_2SO_4 fumes and treat as above directed for an ore.

Notes on the Process.—As a fungus growth forms in the acetate wash, only enough to last a day should be made, unless it is heated frequently.

If the end point be passed in titrating, a few drops of a standard dichromate solution may be added and the titration finished. The iron value of the dichromate multiplied by 1.2363 gives the lead value.

The constitution of the lead chromate depends upon the temperature, acidity and concentration of the solution and the precipitation of the lead from the ore must be made exactly as it is made in the standardization of the thiosulfate.

Bismuth in small amount does not interfere, but if there is much in the sample, some may remain as sulfate with the lead. In such a case, just before filtering off the lead chromate, add 2 grams of citric acid dissolved in a little hot water. This will dissolve any bismuth chromate present.

If the ore contains barium, it is difficult to extract all the lead sulfate with the acetate mixture. In such a case, after the acetate has been used, drop the filter in a flask, add 10 c.c. of strong HCl and boil almost to dryness, add 25 c.c. of the acetate solution, boil vigorously and filter and wash; the combined filtrates are then treated as usual.

Wilders' Modification.—Treat 0.50 gram of ore as is usual for lead ores up to the point where the washed sulfate is obtained on the filter paper. Remove the paper from the funnel and fold lengthwise in such a manner that it can be introduced into a 200-c.c. graduated flask. Place a few grams of sodium acetate and 1 c.c. of acetic acid in the flask and add about 50 c.c. of water. Then place the flask on the hot plate until the lead sulfate is all in solution. This may be hastened by shaking to break up the filter paper.

Now run in an excess of standard dichromate solution from a burette, under the conditions given above and, after mixing by shaking, make the contents up to the mark by adding water. Invert the flask 10 times with the hand over its mouth to mix thoroughly. Take three No. 589 S. & S. filters, fold as one and place in a dry funnel with a dry 100-c.c. flask beneath. Filter 100 c.c. and transfer to an Erlenmeyer flask.

Add a few cubic centimeters of sulfuric acid, enough potassium iodide to react with the excess of chromic acid and titrate with sodium thiosulfate in the usual manner, using starch indicator. The standard dichromate contains 3.558 grams of dichromate per liter. The thiosulfate theoretically contains 8.8177 grams per liter, but 9.150 will be more apt to give the desired strength.

Making the solutions this way, 1 c.c. of dichromate should equal 1 per cent of lead and 2 c.c. of thiosulfate. Therefore, subtracting the cubic centimeters of thiosulfate used from the cubic centimeters of dichromate used will give the per cent of lead direct, without any further calculation.

Notes on the Method.—The chromate solution and the thiosulfate solution are both stable, and once standardized will not require further attention for a month or more. They may be titrated against each other occasionally and restandardized if any variation is found.

The lead chromate precipitate is fine unless boiled, and, therefore, three filter papers are used. The solution filters quickly, however. In methods where the solution is boiled, the lead chromate is of variable composition, depending upon the conditions of precipitation, basic chromates being formed. This method avoids any washing of the chromate and thus saves time and avoids errors due to washing.

REFERENCES:

LOW, "Technical Methods of Ore Analysis."
GUESS, *Trans.* Am. Inst. Min. Eng., **35**, 359.
WADDELL, *J. Ind. Eng. Chem.*, **3**, 638.
WILDER, *Eng. Mining J.*, **92**, 390.

· CHAPTER XXX

THE DETERMINATION OF TIN IN ORES

Tin occurs in ores generally as SnO_2 (cassiterite), sometimes as SnS_2 (stannite). Cassiterite is insoluble in all acids, and to get the tin in solution it is necessary either to fuse the ore with an alkali, forming a stannate which is soluble in acids, or to reduce the SnO_2 at an elevated temperature with either a reducing gas as illuminating gas or with finely divided metal as powdered zinc or aluminium. When the amount of tin is very low and a large sample is used, the reduction of the SnO_2 with a powdered metal to metallic tin followed by solution of the tin in hydrochloric acid is best, because if a large sample is fused with an alkali and the fusion dissolved in acid, the liberated silicic acid causes trouble in filtration. A solution of stannic chloride in hydrochloric acid should not be evaporated, as stannic chloride boils at 114°C.

Tin may be determined gravimetrically by weighing as SnO_2 after precipitation as metastannic acid, or by weighing as the metal after electrolytic precipitation, or, volumetrically,. by titrating the tin in stannous state by a standard oxidizing solution, preferably iodine.

Stannous salts take up oxygen readily from the air, consequently the solution, which is to be titrated, must be protected from the air by a neutral gas, as carbon dioxide.

The following process is the well-known one of Pierce and Low, with the reduction and titration carried out as directed by Patrick and Wilsnack. It depends upon reducing the tin in a strong hydrochloric acid solution in absence of air by means of the combined action of metallic iron and antimony. The tin is reduced to $SnCl_2$, which is then titrated with iodine solution, thus, $SnCl_2 + 2I + 2HCl = SnCl_4 + 2HI$.

Process of Analysis.—Place in an iron crucible about 20 grams of sodium hydroxide and heat over a Bunsen burner until the charge is melted. Cool and add 2.0 grams of the finely ground ore. Cover the crucible and heat cautiously to prevent spattering and, finally, heat with the full flame of the Bunsen until the fusion is quiescent and keep the mass thus fused for about a half hour to insure complete solution of the cassiterite. Cool and dissolve the cake in about 50 c.c. of water and enough HCl to neutralize all the NaOH, and add 50 c.c. additional. When all is in solution, transfer the solution to a 500-c.c. Erlenmeyer flask and add 5 c.c. of sulfuric acid in which is dissolved 0.1 gram of antimony.

Close the flask with a three-hole rubber stopper. Through one hole put a piece of glass tubing reaching to the bottom of the flask, through another place an iron rod, the end of which is coiled into a spiral. The rod should fit loosely enough to slip up and down in the hole in the stopper, and be long enough to have the spiral reach to the bottom of the flask, while the other end sticks out of the stopper several inches.

Push the iron spiral down in the solution and pass CO_2 or natural gas (freed from H_2S by passing through NaOH) through the glass tube until the air is driven out of the flask, and then boil the solution for 25 minutes while continuing the current of gas. Cool the flask while a rapid current of gas passes through to prevent air entering. When the solution is cold, raise the iron coil out of the liquid, wash it by squirting a jet of recently boiled cold water through the third hole in the stopper, put in 4 c.c. of starch solution and then titrate the tin with standard iodine solution by introducing the tip of the burette through the hole in the rubber stopper and running in the iodine solution until a drop turns the starch blue. The iron coil must be so placed that the iodine solution does not drop on it.

Notes on the Process.—When near the end point, which is told by the slow disappearance of the blue color of starch iodide, the titration should proceed slowly to prevent overrunning the end point.

Large amounts of copper, lead, nickel, and perhaps other metals, interfere with the accuracy of the titration if they are present and ores containing them should be first treated with aqua regia, evaporated to dryness, digested with hydrochloric acid and filtered. The residue on the paper is then treated for tin as above directed.

Arsenic and antimony when in trivalent condition consume iodine, if the solution is weakly acid, but in the strong acid solution, as used in this process, they are without effect.

The reduction of the tin is not complete if only iron is used or if only antimony is used, but is perfect if both are used. Some chemists find it satisfactory to use 1 gram powdered Sb and no iron.

Iodine Solution.—To make the iodine solution, put 20 grams of KI and 50 c.c. of water in a liter flask and then add 12.7 grams of pure iodine, stopper the flask and shake the solution until the iodine is all dissolved. Then dilute to a liter and mix well. Standardize against c.p. tin, by dissolving 0.2 gram in a flask in 50 c.c. of water and 50 c.c. of strong HCl. When dissolved, add 5 c.c. of sulfuric acid containing 0.15 gram of antimony and reduce and titrate as directed for ore. Iodine solution of the above strength is tenth-normal and should equal 0.00595 gram of tin per cubic centimeter.

The results obtained are accurate to 0.2 per cent when as much as 0.5 gram of tin is present and much more accurate with the small amounts of tin found in ores.

The disturbing effects of the presence of arsenic, antimony and copper may be avoided by the following modification of the above process:

Proceed exactly as directed above until the HCl solution is obtained after the fusion. Heat the solution to 60°C. and add 4 grams of iron filings to precipitate arsenic, antimony and copper, and to reduce the stannic to stannous chloride. This operation requires about half an hour.

Filter into a 500-c.c. Erlenmeyer flask and wash the residue well with hot water. Heat the filtrate to 95°C. and add 10 grams of pure zinc to precipitate the tin. Drops of the solution should be tested from time to time on a porcelain plate with hydrogen sulfide water. A brown precipitate indicates that tin is still in solution.

When the tin is all precipitated, decant the solution through a funnel containing a plug of glass wool, leaving most of the tin and the zinc in the flask. Put the glass wool with the tin, which was carried over, into the flask. Fit the flask with a two-hole rubber stopper carrying glass tubes for the passage of CO_2. Pass CO_2 through the flask several minutes. Remove the stopper and pour into the flask 30 c.c. of HCl. Replace the stopper and warm the flask gently until the tin and zinc are completely dissolved. Close the exit tube and cool the flask. When cold, disconnect the CO_2 generator, remove the stopper and wash off the tubes with water from which the air has been expelled by CO_2 (1 liter of water+3 grams $NaHCO_3$+HCl), dilute the solution to 250 c.c. with the same water, add a few drops of starch solution and titrate with standard iodine solution.

REFERENCES:

Low, "Technical Methods of Ore Analysis," p. 247.
PATRICK and WILSNACK, *J. Am. Chem. Soc.*, **4,** 597.
GRAY, *J. Chem. Met. S. Africa*, **10,** 312.
MORGAN, *Chem. Eng.*, **14,** 289.
LEWIS, *London Mining J.* (1911), 606; *J. Chem. Met. S. Africa*, **12,** 32 (The electrolytic determination of tin).
MILON and FOURET, *Eighth Intern. Cong. App. Chem.*, **1,** 373.
BOEHMER, GORDON and SIMMONS, *Can. Chem. J.*, **4,** 171.

CHAPTER XXXI

THE DETERMINATION OF ANTIMONY AND ARSENIC IN ORES

Antimony occurs as stibnite (the sulfide) and senarmontite (the oxide), these two minerals constituting the only true ores of the metal. There are, however, many other complex sulfides and oxides in which antimony occurs associated with copper, lead, silver, gold and zinc. While most of the pure antimony employed in commerce is obtained from stibnite, a large percentage is derived from the refining of the base bullion obtained in the smelting of lead ores.

The technical determination of antimony in ores, etc. is best made by volumetric methods. The most troublesome interfering element is usually arsenic. Where arsenic is known to be absent or negligible, the procedure in the following method may be shortened by omitting the operations for its removal. Arsenic is separated from antimony by precipitating as As_2S_3 in a very strongly acid solution.

Most sulfides and mixed ores yield readily to the acid treatment described below, but oxidized ores rich in antimony may fail of complete decomposition. Such material is easily decomposed by the method described on page 222.

When material containing antimony is dissolved by digestion in hot sulfuric acid, the antimony and arsenic go into solution in the trivalent condition and the iron in the trivalent form. If arsenic is absent, the solution can be diluted and titrated with permanganate for antimony. In the presence of arsenic, this direct method cannot be used and arsenic must be separated. The reactions for the titration of antimony are given on page 199.

Process of Analysis.—Weigh 1 gram of the very finely ground ore and transfer to a Kjeldahl flask, add 5 grams of ammonium sulfate, 1 gram of potassium sulfate and 15 c.c. of H_2SO_4 and one-eighth of a 9-cm. filter paper. The paper aids in the reduction of the arsenic and antimony. The ammonium sulfate, by slowly volatilizing, prevents the solution from becoming too hot. Heat cautiously, raising the heat gradually until the H_2SO_4 boils. Continue the heating until the solution becomes practically white and all free sulfur is expelled. Allow to cool while the flask is being rotated. After cooling, add 25 c.c. of water, 25 c.c. of strong HCl and 2 or 3 grams of tartaric acid. Cover the flask with a small watch-glass and warm the mixture, but do not heat to boiling lest some arsenic be lost by volatilization, in case it is to be determined. Boiling would also weaken the acid strength. Maintain fairly hot, with occasional agitation, until the solution is as complete as possible. Anhydrous ferric sulfate will dissolve more quickly if a little ferrous sulfate be added. Now add 25 c.c. more of cold strong HCl and then pass in hydrogen sulfide until any arsenic present is completely precipitated. As the arsenic is in the "*ous*" condition, this will take only a short time, perhaps 10 minutes. Some copper may be precipitated, but no antimony or tin. Filter through a double 9-cm. filter which has been moistened with 2:1 HCl. Use an ordinary suction funnel. A platinum cone will insure the filter from breaking. Rinse off the delivery tube with 2:1 HCl and remove it. Rinse out the flask several times with the same acid mixture, and wash the precipitate with it also at least six times. Receive the filtrate in a large beaker. If arsenic is to be determined, reserve the precipitate, and any particles adhering to the flask and delivery tube.

Dilute the filtrate with double its volume of warm water and saturate it with hydrogen sulfide. Simple dilution will cause a precipitation of antimony sulfide, but it is not safe to omit passing the gas also. Filter off the precipitate, which may consist of antimony sulfide mixed with other sulfides, and wash it from six to ten times with hydrogen sulfide water, so as to remove nearly all the chlorides. Use an 11-cm. filter. With a jet of hot water, using as little as possible, wash most of the sulfide from the filter into the beaker. Add a little colorless sodium sulfide solution and warm to effect the solution of the antimony sulfide. Pour through the last filter, and wash filter and residue well with hot water containing a little sulfide. One extraction will usually suffice. Receive the filtrate in a Kjeldahl flask. Small amounts of antimony sulfide may be dissolved directly on the filter. To the filtrate add 2 grams of potassium sulfate and about 8 c.c. of strong H_2SO_4. (The addition of organic matter for reduction is here unnecessary.) Boil as previously described to expel, first, the water, then all the free sulfur and, finally, most of the free acid. Small amounts of chlorine appear to be harmlessly expelled before the antimony sulfide is decomposed. Cool with the flask inclined. Add to the residue 50 c.c. of hot water and 10 c.c. of strong HCl. Heat to effect solution and then boil for a short time to expel any possible sulfur dioxide. Finally, add 10 c.c. more of strong HCl, cool under the tap, dilute to about 140 c.c. with cold water and titrate to the usual pink tinge with a standard solution of potassium permanganate. The solution ordinarily used for iron titrations (2.83 grams per liter) will answer. The iron value of the permanganate multiplied by 1.075 will give the antimony value. A small amount of copper (frequently present) has no influence on the titration. If the solution becomes turbid before or during the titration, add a few grams of tartaric acid to clarify it. Standardize the $KMnO_4$ as directed on page 196.

Sometimes an appreciable amount of undecomposed material remains after the above acid treatment of the substance. If this is likely to contain antimony it may be further treated as follows: Proceed as described until after the first filtration, thus obtaining the undecomposed residue and any arsenic sulfide on the filter. Reserve the filtrate and continue with the material on the filter as described for arsenic until the latter is removed, omitting this step, of course, if no arsenic is present. Ignite the thoroughly washed filter and residue at a low temperature in a thin iron crucible until the carbon is all burned off, and then fuse with a little sodium hydroxide. Dissolve the melt in hot water, transfer to a beaker, acidify with HCl, and add the solution to the reserved filtrate. Continue with this as described.

Arsenic.—Treat 0.5 gram of the ore precisely as described for the determination of antimony up to the point indicated in the text where the arsenic is obtained on the filter as sulfide, the antimony being in the filtrate. Now proceed as follows:

Rinse out any sulfide adhering in the flask or on the delivery tube as completely as possible, pouring through the filter, and then wash the filter and contents well with hydrogen sulfide water. Absolutely complete removal of the HCl is unnecessary. Dissolve the arsenic sulfide (this may usually be done directly on the filter) and also any particles of sulfide on the delivery tube with warm ammonium sulfide solution and wash with the same solution diluted, receiving the filtrate in the original flask. To the filtrate add 1 gram of potassium sulfate, 3 grams of ammonium sulfate, and 8 c.c. of strong H_2SO_4. Boil the mixture to a small bulk and then manipulate the flask over a free flame until all the sulfur is expelled and a clean melt of mixed sulfates is obtained. Cool with the flask inclined as a precaution against cracking. Any small amount of HCl present is expelled during the heating before the arsenic sulfide is decomposed, and, therefore, causes no loss of arsenic by volatilization as chloride. Take up the cool residue by warming with 50 c.c. of water and then boil a short time to expel any possible sulfur dioxide. Now cool to room temperature, add a little starch solution, then, with a little phenolphthalein as indicator, make slightly alkaline with a solution of sodium hydroxide and again reacidify slightly with HCl. Cool once more if necessary. Finally, add 3 to 4 grams of sodium acid carbonate and titrate with standard iodine solution. Pay no attention to a brownish discoloration toward the end, but proceed slowly until a single drop of the iodine solution produces a strong permanent blue color. If neutral starch liquor is used it need not be added until just before titration.

The iodine solution may be prepared by dissolving about 11 grams of iodine in a little water, with the addition of about 20 grams of potassium iodide, and diluting to 1 liter. Standardize with pure powdered arsenious oxide. Dissolve about 0.150 gram by warming gently in an 8-oz. flask with a little sodium hydroxide solution. Dilute somewhat, cool, add starch, neutralize, etc., similarly to the above, and finally titrate with the iodine solution. One cubic centimeter of the latter will equal about 0.003 gram of arsenic. Multiply the weight of As_2O_3 taken by 0.7575 to obtain the equivalent weight of As.

A small amount of copper is without influence in the titration, provided it remains in solution. If a precipitate of copper arsenite is formed, add a little ammonium chloride to dissolve it. The reaction for the titration of arsenic is

$$Na_3AsO_3 + 2I + H_2O = Na_3AsO_4 + 2HI$$

REFERENCES: WEIRICH, *Chemist Analyst*, no. 30 (crude arsenic). LOW, *J. Am. Chem. Soc.*, **28,** 1715. KRICKHAUS, *Eng. and Min. J.*, **90,** 357. LOW, "Technical Methods of Ore Analysis."

CHAPTER XXXII

DETERMINATION OF MERCURY IN ORES

The mineral cinnabar (HgS) is the chief ore of mercury. It is also found native and amalgamated with silver.

The mercury may be extracted from the ore by wet methods or by distillation. When distilled from the ore, the mercury vapor is usually condensed on metallic gold, with which it amalgamates, and the increase in the weight of the gold is taken as the mercury in the sample. Iron filings are used to keep sulfur from going over with the mercury. Instead of condensing the mercury on gold, it may be condensed in water and weighed after being dried. When mercury is determined by wet methods, the mercury may be precipitated electrolytically or precipitated and weighed as a sulfide or titrated with a KCNS solution or titrated with standard KI solution.

The most satisfactory procedure seems to consist in the cominbation of the distillation and titration methods.

When mercury sulfide is heated in the presence of lime and copper oxide, the mercury is distilled free from sulfur. Many mercury ores contain considerable bituminous or other organic material which will distil partially with mercury.

The distillation of mercury from its ores is very accurate and reliable. When the material contains chlorides or sulfates it should be mixed with iron filings to reduce these compounds. The titration of mercury with a standard KCNS solution in the absence of halides is very accurate and is not interfered with by the presence of Cu, Zn, Cd, Sn, Pb, Th, As, Sb, Bi, Mn and Fe. Silver titrates the same as mercury but is separated by the distillation process.

Process of Analysis.—Prepare a distillation tube by sealing one end of a hard glass tube about 12 in. long and 0.4 in. in diameter. Pour about ½ in. of coarse sand into the tube. Weigh 1 gram of the finely powdered ore, place in a small casserole and add 1 gram of powdered copper oxide and ½ gram of dry lime. Mix these materials thoroughly in the casserole and pour them through a funnel into the tube. Sprinkle a little lime into the casserole and brush the lime with what traces of ore may have stuck to the casserole through the funnel and into the tube.

Add ½-in. layer of lime and about the same amount of 20-mesh sand and then push into the tube a plug of brass gauze which fits tightly enough into the tube so that when the tube is held upside down none of the materials falls out. The plug is made by rolling a piece of brass gauze into the shape of a cylinder with a diameter equal to the inner diameter of the glass tube, and folding in at one end to close it. It it well to make a spring of nichrome wire which, when placed in the gauze cylinder, will hold it tightly in the glass tube. Push the gauze plug tightly against the charge in the tube.

Place the tube in a furnace previously heated to 500°C. and continue the heating for 15 minutes. (A convenient furnace is an iron block with a hole drilled in it long enough to take the tube up to the gauze plug.)

Withdraw the tube and place it open end down in a test-tube containing 5 c.c. of hot HNO_3. When the tube has cooled, sufficiently for handling, break off the bead at the fused end of the tube, attach a piece of rubber tubing and suck the hot acid into the tube until it is above the ring of condensed mercury, taking care that the HNO_3 solution does not come in contact with the brass plug. If the acid is hot, the mercury dissolves quickly, but cold acid dissolves it very slowly. When the mercury is completely dissolved, pour the solution into a 100-c.c. beaker. Add distilled water to the test-tube and suck it into the distillation tube to wash out mercuric nitrate. Repeat the washing with fresh distilled water, transferring the washings to the main solution.

Add strong permanganate solution until a permanent color is obtained to oxidize the mercury, and then destroy the excess of permanganate with a drop or two of H_2O_2. The volume should now be about 30 c.c. and the solution cool. Add 2 c.c. of 10 per cent ferric nitrate (there must be absolutely no halide present). Add slowly and carefully a standard solution ($0.1N$ to $0.01N$) of KCNS. As soon as the mercury is all changed to HgCNS the addition of another drop of the solution brings a distinct pink, which is the end point. This pink is due to the formation of ferric sulphocyanate.

Standardize the sulfocyanate solution by dissolving a carefully weighed amount of purified mercury in 5 c.c. of HNO_3, oxidizing with permanganate and proceeding as above.

Notes.—The distillation tube should have the closed end drawn down so that it can be easily broken and a rubber tube attached.

The tube is inserted into the furnace just far enough to have the gauze plug in the furnace. The end of the tube must be sufficiently out of the furnace to assure complete condensation of mercury.

If the ore does not contain sulfur, the copper oxide can be omitted.

The ore may be first dissolved in HNO_3, the mercury precipitated with H_2S after near neutralization and the HgS so obtained treated as above.

Before the distillation tube is inserted in the furnace, it should be tapped a little to afford a channel for the passage of mercury, the tapping being done while the tube is lying on its side.

If the ore contains organic matter, it is well to put about 0.10 gram of $KClO_3$ in the bottom of the tube with the sand. When chlorate is used, the tube should be heated slowly from the gauze plug back toward the closed end.

REFERENCES:

BOUTON and DUSCHAK, *Tech. Paper* 227, U. S. Bureau Mines.
PLACE, *Eng. Mining J.*, **109**, 1313.
LOW, *Chemist-Analyst*, **29**, 13.

CHAPTER XXXIII

DETERMINATION OF BISMUTH IN ORES AND ALLOYS

Bismuth is determined both in ores and alloys. The ores of bismuth contain the sulfide, bismuthinite (Bi_2S_3), native bismuth, bismutite ($BiOBi(OH)_2CO_3$) and many less important minerals. The alloys which contain bismuth are chiefly the easily fusible alloys. The principal source of bismuth in the United States is the residues from lead refining.

Bismuth is usually precipitated for weighing, as BiOCl, from an acid solution. It is separated from iron and aluminium, etc. by precipitation with H_2S. Bismuth sulfide is separated from arsenic, antimony and tin by digestion with alkaline sulfide and from copper by digestion with KCN.

Process of Analysis.—Weigh 1 gram of the finely ground ore, transfer to a casserole and add 10 c.c. of HNO_3, evaporate nearly to dryness, add 5 c.c. of HCl and digest until solution is as complete as possible. Add 10 c.c. of H_2SO_4 and evaporate until fumes of SO_3 are copiously evolved. Cool, add 25 c.c. of water and heat and stir for several minutes until all bismuth sulfate is dissolved. (Lead sulfate remains insoluble.) Filter and wash with 1:10 H_2SO_4 promptly. If allowed to stand too long, basic bismuth sulfate may separate. Dilute to 75 c.c. and precipitate with H_2S until the solution is saturated with H_2S. Filter and wash with H_2S water. Wash the precipitate back into the beaker and add 4 grams of pure KCN and warm and stir for a long time. Bismuth and cadmium sulfides remain undissolved. Filter through the same filter as before and wash well with hot water. Place the filter and precipitate in a 250-c.c. beaker, add 10 c.c. of 1:2 HNO_3 and heat until the sulfides are all dissolved, add 20 c.c. of water and filter through a Gooch crucible without additional filter paper and wash thoroughly with 1:2 HNO_3. Dilute to 300 c.c., heat to boiling and add dilute ammonia cautiously until the solution becomes slightly cloudy. Add 1 c.c. of 1:3 HCl and keep hot for an hour or more. The bismuth precipitates as

BiOCl. Filter on an asbestos mat in a Gooch crucible dried at 105°C. and weighed. Wash the BiOCL with hot water, dry at 105°C. and weigh. The BiOCL multiplied by 0.8017 gives the weight of the bismuth. The precipitation reaction is $BiCl_3 + H_2O = BiOCl + 2HCl$.

Notes.—If there are any AsO_4, PO_4 or many SO_4 ions present, the bismuth will be contaminated with them.

Some chemists prefer to pour the nitric acid solution of bismuth into water containing a little HCl.

Bismuth may also be determined as oxide or phosphate or metal.

Volumetric determinations of bismuth are not very satisfactory and electrolytic determinations are quite unsatisfactory.

REFERENCES:

PRICE and MEADE, "Technical Analysis of Brass."
IBBOTSON and AITCHISON, "The Analysis of Non-ferrous Alloys."
LOW, "Technical Methods of Ore Analysis."
HEATH, "Analysis of Copper."

CHAPTER XXXIV

THE DETERMINATION OF COPPER IN ORES

Most copper ores are soluble in strong mineral acids. In dissolving an ore it is best to treat first with hydrochloric acid to dissolve oxidized minerals, then with nitric acid to dissolve sulfide minerals. Slags may require fusion with $NaCO_3$ or treatment with HF.

The chief minerals of copper are native copper, chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), bornite (Cu_5FeS_4), tetrahedrite ($4Cu_2SSb_2S_3$), cuprite (Cu_2O), malachite (basic carbonate), azurite (basic carbonate), chalcanthite and brochantite (sulfates) and many others.

There are many methods for the determination of copper, of which four are the most widely used. They are the iodide, electrolytic, cyanide and thiocyanate methods. The electrolytic method is the most accurate for use on ores which do not contain arsenic, antimony or bismuth, but for analyzing these impure ores or miscellaneous ores the nature of which is not known, the iodide method is the most applicable, because it is accurate and rapid, and the above elements do not interfere.

THE IODIDE METHOD FOR COPPER

This method depends upon the fact that in a solution slightly acid with acetic acid, cupric compounds oxidize potassium iodide with the liberation of iodine. This is then titrated with a standard thiosulfate solution. The reactions are:

$$Cu(NO_3)_2 + 2KI = CuI + 2KNO_3 + I$$

and

$$2I + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6.$$

The copper iodide is precipitated as a white precipitate. The titration is accurate and the end point sharp. Of course, there must not be anything present, besides copper, which will liberate or absorb iodine. Nitrous oxides, ferric ions, free bromine, trivalent arsenic and trivalent antimony must be absent, as they will either absorb or liberate iodine. Excess of free mineral acids must not be present. Pentavalent arsenic and antimony do no harm. Bismuth and lead, if present in solution, cause some trouble by making it difficult to see the end point, owing to the formation of yellow iodides, but otherwise cause no trouble. The following method can be much shortened by using the modification on page 232.

Process for Ores.—Take enough of the finely ground ore for a sample, so that there will be present from 0.05 to 0.40 gram of copper. Put in a 250-c.c. beaker and add 7 c.c. of concentrated HCl and heat. Then add 10 c.c. of strong HNO_3 and heat until the ore is completely decomposed. Then add 7 c.c. of strong H_2SO_4 and evaporate until the sulfuric acid fumes strongly. Cool and add 30 c.c. of water and heat until all soluble salts are dissolved. Cool, add 4 grams of granulated zinc and shake for several minutes. The copper will be quickly precipitated. Heat until the zinc is dissolved, then add 25 c.c. of H_2S water to make sure that the last traces of copper are precipitated. Filter and wash several times to remove all iron salts. Wash the precipitated copper back into the beaker with a jet of water, using not more than 10 c.c. of water if possible, in order to avoid having a dilute nitric acid solution. Add 7 c.c. of strong HNO_3, heat until all copper goes into solution and boil until nitrous fumes are expelled. Then pour the hot solution through the filter paper, wash the paper with 5 c.c. of bromine water to dissolve any copper sulfide there. Finally, wash the beaker and paper thoroughly with water. The bromine also oxidizes any nitrous oxide and arsenic or antimony present.

Heat the filtrate to boiling and boil vigorously for not less than 10 minutes to expel all bromine. Cool and add ammonia or sodium hydroxide until the solution turns blue or becomes just alkaline. Do not add an excess of alkali. If an excess is added, drop in a few drops of sulfuric acid until the excess is neutralized, then add alkali again. Now add acetic acid until the liquid becomes acid, then add 2 or 3 c.c. of 80 per cent acetic acid in excess. Cool to tap-water temperature.

Dissolve 3 grams of KI in a few cubic centimeters of water, add it to the solution to be titrated and stir well. It immediately becomes brown, due to the liberated iodine. From a burette run the standard thiosulfate solution in until the brown color is nearly gone, then add 5 c.c. of starch solution. Continue the addition of the thiosulfate carefully until 1 drop turns the solution from a blue to a white or yellowish-white. This is the end point. It should be stable and the blue color should not reappear upon standing five minutes. If the blue reappears, it indicates faulty work. If the solution is not sufficiently acid, the end will not be sharp.

Standardization of the Thiosulfate.—Dissolve 19.55 grams of pure $Na_2S_2O_3.5H_2O$ in water, add 1 gram of NaOH and dilute to 1 liter. The water should be free from CO_2, and the solution should be kept in the dark. Also make a starch solution as directed on page 97.

Weigh carefully about 0.2 gram of pure copper wire or foil. Place in a 250-c.c. beaker and dissolve in 10 c.c. of 1:1 HNO_3. Dilute to 25 c.c., boil off the red fumes, then add 5 c.c. of bromine water and boil about 10 minutes, or until the bromine is all expelled. Remove from the heat, dilute to 75 c.c., add NH_4OH until the solution becomes just alkaline (becomes blue) but not more. Add acetic acid until the solution becomes acid, then 2 c.c. more of strong acetic acid. Cool to tap-water temperature, add 4 grams of KI dissolved in 15 c.c. of water and stir a moment. Now run in the thiosulfate solution from a burette until the yellow color of free iodine has nearly gone and then add 5 c.c. of starch solution. This should produce a marked blue color. Continue the titration cautiously until on the addition of another drop the blue color of starch iodide disappears. There should be no difficulty in locating the end point within a single drop. One cubic centimeter of the thiosulfate solution should be equal to 0.005 gram copper.

Notes on the Process.—Aluminium may be used in place of zinc to precipitate the copper, but zinc acts more rapidly and certainly. It is possible to precipitate all the copper with the zinc, but is best to add the hydrogen sulfide always, to make sure of complete precipitation. Of course, arsenic, antimony, silver, bismuth, etc. also precipitate. Lead remains insoluble as lead sulfate.

The addition of bromine water is absolutely necessary in analyzing ores containing arsenic or antimony, in order to oxidize them to the pentavalent state. If they are not so oxidized, the iodine liberated by the copper will be used up in oxidizing arsenic and antimony from trivalent to pentavalent condition. The bromine also insures complete solution of the copper sulfide and absence of nitrous oxides. Excess bromine must, of course, be boiled off.

It is necessary to use a large excess of KI to hold the liberated iodine in solution and make the reaction rapid; 5 grams per 100 c.c. are needed.

Lead and bismuth having yellow iodides cause trouble, if present, by making it very difficult to tell when to add the starch, but with experience this is not a serious trouble. No other elements cause trouble.

Molybdenum would interfere if in the solution being titrated, but the zinc separates copper from molybdenum.

It is necessary that the acetic acid be added to a solution not too alkaline, as the acetate formed on adding the acid to an alkaline solution decreases the ionization of the acetic acid (according to the mass action law), thus making the solution insufficiently acid for the reaction between the copper and the iodide to be complete, causing an indefinite end point.

If the end point is overrun, simply add 1 c.c. of a copper sulfate solution containing 0.01 gram of copper per cubic centimeter, then complete the titration and subtract 0.01 gram from the total amount of copper found.

When the ore contains arsenic or antimony, it is necessary to use bromine after the solution of the ore has been evaporated to sulfuric acid fumes, for, even if the ore is dissolved in aqua regia, after evaporation to fumes of sulfuric acid the arsenic and antimony are present as the trivalent elements. The volume of the solution should be kept less than 100 c.c.

SHORT IODIDE METHOD FOR COPPER

The following process is a modification of the process of Mott.[1] The process is very rapid and, according to the writer's experience, the results obtained by its use are nearly as good as by the long iodide method.

The copper is not separated from the other metals. This makes it necessary to remove any ferric ions which, if present, would liberate iodine and cause results to be high. These ferric ions are removed by adding ammonium fluoride, which forms, with the iron, undissociated ferric fluoride, which, since it is undissociated, has no oxidizing power and cannot liberate iodine under the conditions of the solution.

Process of Analysis.—Dissolve a sufficient sample of the ore in 5 c.c. of strong HCl and 7 c.c. of HNO_3, heating the solution to boiling. When action has ceased, add 10 c.c. of 1:1 H_2SO_4 and evaporate rapidly until the sulfuric acid fumes strongly. Cool and add 30 c.c. of water, heat until all soluble salts are in solution, then add 5 c.c. of bromine water and boil vigorously for 10 minutes or until all bromine has gone. Now add NH_4OH

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[1] *The Chemist-Analyst*, July. 1912.

until ferric hydroxide persists on shaking, then add 2 or 3 c.c. of 80 per cent acetic acid, cool to tap-water temperature, add 2 grams of NH_4F and stir until it is dissolved. The ferric hydroxide will immediately dissolve, but the solution will be turbid. Add 2 grams of KI dissolved in water and titrate as usual.

Notes on the Process.—The thiosulfate should be standardized by dissolving 0.20 gram of copper and about 0.10 gram of iron in nitric acid and treating the solution exactly like an ore solution.

After the titration is finished, the solution should be emptied out of the beaker, as the beaker will be etched by the HF on long standing.

The writer has used this method on samples containing 10 per cent of iron, 5 per cent arsenic, and 7 per cent antimony, with perfect results, when compared with the long iodide method.

The writer often combines the sulfocyanate precipitation with the thiosulfate titration.

REFERENCES FOR THE IODIDE METHOD:

PETERS, *J. Am. Chem. Soc.*, **34,** 422 (sources of error in standardization).
VIDEGREN, *Z. anal. Chem.*, **48,** 539.
MCCLURE, *Mining Sci. Press*, **103,** 48.
LATHE, *Eng. Mining J.*, **93,** 1073 (methods used at Granby).
GOOCH and HEATH, *Am. J. Sci.*, **24,** 65.
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THE ELECTROLYTIC DETERMINATION OF COPPER IN ORES, ETC.

The electrolytic precipitation of copper is the most accurate method of determining copper when the conditions are right. Ores containing arsenic, antimony, bismuth, or selenium or tellurium are, perhaps, not best analyzed by the electrolytic method. It is true that the electrolytic separation of copper from these elements can be made, but the methods are not usable technically. So if these interfering elements are present, they must be separated by purely chemical methods before the copper is electrolyzed. Methods involving delicate adjustment of potential for the separation of elements, while interesting from a scientific standpoint, are too troublesome to be used in technical analysis; the only electrolytic methods used are those in which separation depends upon choice of electrolyte; some elements will separate from acid solutions, some will not. Some will separate from sulfide solutions, some will not. Thus copper can be separated electrolytically from iron, aluminium, zinc, etc., from a dilute nitric or sulfuric acid solution.

The deposition of copper should take place from a solution free from hydrochloric acid (except under special conditions), free from interfering elements, and not too acid with either nitric or sulfuric acids. It is important that the current density at the cathode be not too great. The current density depends upon the size of the cathode, the distance between the electrodes, the conductivity of the solution and the drop of potential between the electrodes. If the current density be too great, the copper will deposit in a non-adherent condition.

If the solution is kept vigorously stirred, so that the copper ions are kept coming in contact with the cathode rapidly, the precipitation of the copper is more rapid and the current density employed may be much greater without getting a poor deposit. If a gauze cathode is used, an enormously greater current density may be used than if a plain cathode be used. A plain flat cathode should be sand-blasted or roughened in some way so that the copper deposit will be more adherent.

If two platinum plates or electrodes be dipped into a conducting solution or electrolyte and the two electrodes be connected externally through a source of direct-current e.m.f., a current will pass through the solution. If the e.m.f. is below a certain voltage the current will pass only momentarily, because electrochemical action at the electrodes causes the liberation of material at the electrodes which sets up a back or polarization e.m.f. equal to the applied e.m.f. If the voltage is increased gradually, a potential will finally be reached at which the applied e.m.f. is greater than the back or polarization e.m.f. (and resistance of the solution) and a current will continually pass with liberation of material at the electrodes. The material which precipitates at the electrodes will be that element or that radical which has the lowest back e.m.f. (osmotic pressure disregarded). If the conditions of solution are such that the back e.m.f. or solution tension is greater for the metal the deposition of which is desired than for the decomposition of water, the electric current will be used or wasted in liberating hydrogen and oxygen rather than for the precipitation of the metal. Hence, it is necessary so to select the reagents in the solution that the solution tension or back e.m.f. of the metal is below the decomposition e.m.f. of water. If there be several elements present the back e.m.f. of which is less than that of water, or not greatly above it, they will be precipitated by the current simultaneously if the e.m.f. is high enough. By very careful regulation of the potential it is possible to make quantitative separation of some metals from each other, that is, by using a voltage higher than that required to precipitate one of the metals and lower than that required to precipitate the others present. The e.m.f. required varies with various kinds and concentrations of solution, owing to the different "solution tensions" of metals in different solutions.

It is possible to separate some metals, such as copper and lead, by taking advantage of the fact that in certain solutions one metal can be deposited as metal on the cathode and the other as oxide on the anode. There is a definite quantitative relationship between the amount of metal precipitated and the quantity of electricity used. This is expressed in the following general way: 96,550 coulombs (ampere-seconds), if used under ideal conditions, will accomplish unity valence change to the gram atomic weight of any element. Thus, 96,550 coulombs, or 1 amp. passing for 96,550 seconds, will deposit the gram atomic weight of silver or one-half the gram atomic weight of copper.

Each metal which is precipitated electrolytically requires certain definite conditions as to voltage, current density, nature and concentration of electrolyte, absence of certain foreign elements, and temperature for satisfactory electroprecipitation.

Method for Ores Free from Arsenic, Antimony and Bismuth.—Use for a sample an amount of ore which will contain not more than 0.20 gram of copper. The sample must be finely ground. Put in a 150-c.c. beaker and add 15 c.c. of a mixture of equal parts of HNO_3 and HCl. Heat until decomposition of the ore is complete. Add 4 c.c. of H_2SO_4 and evaporate to copious fumes of SO_3. Cool, add 25 c.c. of water and 5 c.c. of HNO_3 and heat until all soluble salts are dissolved. Dilute to 125 c.c. and filter if the residue is such as not to settle clear. If it settles well, it is not necessary to filter. The solution is now ready for electrolysis. If silver is present, add just enough NaCl solution to precipitate it.

The details of the electrolysis will depend upon the nature of the cathode. If a plain electrode is to be used, add 1 c.c. of the "nitro preparation";[1] if a gauze electrode is used, it is not needed. Connect to a suitable source of electric potential and adjust the rheostat until the proper current density on the cathode is attained. If a plain cathode is used, the current density should be from 0.1 to 0.5 amp. per 100 sq. cm. of surface, depending upon the roughness of the surface and amount of copper to be deposited. The rougher the surface and the less the copper present the greater the current density which may be employed. With a plain electrode, the time required will be from four hours to

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[1] The "Nitro preparation" is made by G. A. Guess as follows: Warm 10 grams of No. 4 hard oil or vaseline with 100 c.c. of strong HNO_3 until the action ceases, then dilute to 300 c.c. and filter.

overnight, unless the solution be continually stirred. If the solution be kept agitated, the time required may be greatly reduced. If a gauze cathode be used, the electrolysis may be completed in from 15 minutes to an hour with a current of 5 amp. without the trouble incident to a mechanical stirrer or solenoid and still beautiful and adherent deposits of copper are obtained. The writer uses gauze cathodes and has abanonded mechanical stirring of the solution as being unnecessary and troublesome. If stirring of the solution be done, it is best to use a rotating magnetic field produced by a Frary solenoid.

Continue the passage of the current until the copper seems all precipitated, then withdraw ½ c.c. with a pipette and add it to a similar amount of H_2S water on a paraffined white plate. (The liquid will not run on the paraffined plate.) If the slightest amount of copper remains, the test will darken. If the test shows that the copper is all precipitated, lift the cathode quickly out of the solution and set in a beaker of distilled water. Then wash it with alcohol, dry on a steam plate or in an oven at about 100°, cool and weigh. The copper should be crystalline and beautifully bright and too firm to be scratched off with the finger nail. If it is firm but dull in color it indicates the presence of one of the interfering elements. The precipitate may be dried by moistening it with alcohol and setting fire to the alcohol (see page 184). The weight of the cathode and copper minus the weight of the cathode divided by the weight of the sample, then multiplied by 100, gives the percentage of copper in the sample.

REFERENCES:

SPILLSBURY, *Eng. Mining J.*, **84,** 773 (short method using "nitro").

GUESS, *Eng. Mining J.* (1906), 328 (electrolytic assay for Pb and Cu).

HEATH, *J. Ind. Eng. Chem.*, **3,** 73 (exact electrolytic assay of copper).

TRAPHAGEN, *Chem. News*, **104,** 69.

CAVEN and CHADWICK, *Eng. Mining J.*, **89,** 954 (electrolytic methods for slags, ores, mattes and blister copper).

BENNER, *J. Ind. Eng. Chem.*, **2,** 195; *Met. Chem. Eng.*, **9,** 141 (use of gauze cathode in technical analysis).

SCHOCH and BROWN, *J. Am. Chem. Soc.*, **28,** 1660.

The source of the electric current may be a direct-current power line or storage batteries or primary cells or an alternating-current power line. If a direct-current power line is used, all that is necessary is a proper rheostat and ammeter in series with the electrolysis cell. If direct-current line is not available, but an alternating-current is, it may be used in connection with a chemical rectifier or a motor generator set. Storage batteries are very convenient, especially when only alternating-current power is available and it is not desired to keep a rectifier running continuously. The writer uses a chemical rectifier in connection with alternating current to charge storage battery from which current for electrolysis is obtained. The rectifier cost about $10 to build and has been in service for several years with perfectly satisfactory results. It is shown in Fig. 11.

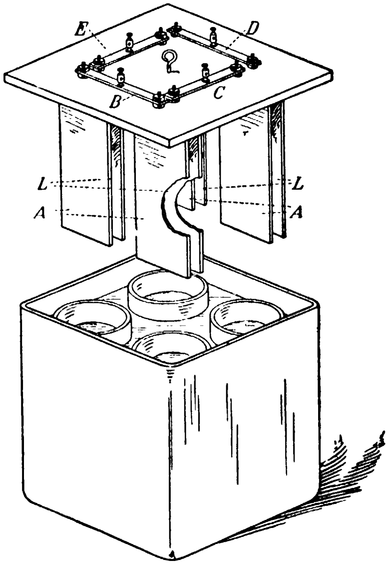

FIG. 11.

A–A–A–A are aluminium plates 10 × 4 in. in size. *L–L–L–L* are lead plates of the same size. These plates are attached to brass rods which pass through a hard rubber board, and are fastened by nuts to the bars *B*, *C*, *D* and *E*. To bar *B* are attached two aluminium plates, to bar *C* are attached a lead and an aluminium plate, to bar *D* are attached two lead plates, and to bar *E* are attached a lead and an aluminium plate. The alternating terminals are on the bars *C* and *E*. The direct-current terminals are on the bars *B* and *D*. The plates hang in the jars *J–J–J–J*, which are filled with a saturated ammonium phosphate solution. The jars set in a tank of water to keep them cool. The alternating-current impulses cannot pass through the solution from aluminium plates to lead plates, but can pass from lead plates to aluminium plates. Thus, both of the alternating-current impulses are sent in the same direction out from bar *B*, to do whatever work is desired, and returned through bar *D*. The alternating potential between *C* and *E* must not be greater than 25 volts.

By far the most convenient arrangement for electroanalysis is a small motor generator set and storage cells. When large numbers of electroanalyses are made, a cabinet in which as many as fifty electroprecipitations may be carried on at once, may be obtained from manufacturers.

Method for Impure Ores.—Ores containing arsenic, antimony or bismuth cannot be electrolyzed for copper without first separating the copper from these elements by purely chemical means. The following method makes the separation by one filtration and gives accurate results. It depends upon the fact that cuprous copper may be precipitated completely and free from the above elements by means of potassium thiocyanate (KCNS) from a solution slightly acid and containing tartaric acid. The CuCNS is dissolved and electrolyzed after the thiocyanic acid is destroyed.

Process of Analysis.—Dissolve a sufficient weight of the sample in 7 c.c. of HCl and 7 c.c. of HNO_3. When the ore is decomposed, add 5 c.c. of H_2SO_4 and evaporate to fumes of H_2SO_4. Cool and add 25 c.c. of water, in which are dissolved 3 grams of tartaric acid, and heat until all soluble salts are in solution. Filter and wash the residue well with water. Add NH_4OH until the solution becomes alkaline, then add H_2SO_4 until the solution is acid, then 1 c.c. in excess. This makes the solution slightly acid with tartaric acid. Now add 4 grams of Na_2SO_3 to reduce the copper to the monovalent ion, heat nearly to boiling and add 1 gram of KCNS dissolved in water. The CuCNS precipitates immediately as a dense white precipitate but the solution will be colored red if there be trivalent iron present. This does no harm. Stir well and allow the CuCNS to settle for several minutes. Then filter through a close filter and wash five times with a warm solution containing a little KCNS and tartaric acid.

Place the paper and contents in a porcelain crucible and ignite at low temperature to burn off the paper. Transfer the copper oxide to a 100-c.c. beaker and dissolve with 5 c.c. HNO_3. When dissolved, dilute with 75 c.c. of water, add 1 c.c. of H_2SO_4 and electrolyze as directed on page 235.

Notes.—This separation of copper from impurities is very satisfactory and may be used for the iodide method as directed on page 230. In fact, for miscellaneous unknown ores which come to this laboratory this method of separation is preferred.

It is absolutely essential that the HCNS be completely destroyed before electrolysis, as its presence ruins the electrolytic determination. The simplest way of destroying it is by ignition. Mere solution in HNO_3 does not destroy the HCNS. Long boiling is required, or the addition of bromine or ammonium persulfate, which, in turn, have to be destroyed.

It should be emphasized that electrolytic determinations are much more satisfactory with gauze electrodes than other kinds. The writer uses a gauze cathode of cylindrical form, 1 in. in diameter and 2.5 in. high, and a current of 2 amp. for 10 minutes, then a current of 4 amp. until the precipitation is complete as shown by a test on a white plate with H_2S. Precipitation is complete in one-half hour to an hour. Set the cathode quickly into a beaker of distilled water, then wash with alcohol, dry at 100° and weigh.

The tartaric acid is added to keep antimony in solution and because the presence of tartaric acid is desired when the copper is precipitated. If the ore contains lead, the sulfate formed goes into solution when the tartaric acid is neutralized if it is not filtered off.

If the lead is in solution, some of it precipitates when the sulfite is added and is left on the paper when the CuCNS is dissolved, but this does no harm, as it precipitates on the anode during electrolysis, nor does the presence of large amounts of ferric iron. The writer has precipitated 0.2 gram of copper from 0.2 gram of iron, 0.1 gram of arsenic, 0.1 gram of antimony and 0.1 gram of bismuth and large amounts of lead, and always obtained excellent results, correct almost to the limit of error of weighing on an ordinary analytical balance.

It is necessary to destroy the HCNS because the copper precipitates by electrolysis in a very spongy condition if there is HCNS in solution.

Under the conditions given above, one fully charged lead storage cell without a rheostat in series will give a drop of potential between the electrodes of 2 volts and a current of $\frac{2}{5}$ amp. Two cells will give a drop between the electrodes of about 3 volts and a current of 3 amp. and three cells of 10 amp. capacity a drop of 3.5 volts and 5.5 amp., and when a gauze cathode is used a rheostat is not necessary to reduce the current. A vacuum tube rectifier is very satisfactory.

REFERENCES:

DEMOREST, *J. Ind. Eng. Chem.*, **5,** 216.
TSUKAKOSKI, *Eng. Mining J.*, **90,** 969.

The Guess-Haultain electrolytic cabinets are made so that 200 or more determinations may be made in a day.

For the methods of electrolytic separation of copper from arsenic, antimony, bismuth, silver, mercury and other elements, see "Electro-analysis," by E. F. SMITH and "Practical Methods of Electrochemistry," by F. M. PERKIN.

THE CYANIDE METHOD FOR COPPER IN ORES

When a nitric acid solution of copper is made alkaline with ammonia, it becomes intensely blue, owing to the formation of the compound $Cu(NH_3)_4(NO_3)_2$. When a solution of KCN is added to this blue solution, it becomes less and less blue and finally colorless, owing to the formation of colorless $K_6NH_4Cu_2(CN)_8$,[1] the copper thus changing from a part of a colored cation to a part of a colorless anion in which it is univalent.

The amount of KCN required to titrate a copper solution depends upon the temperature of the solution, the volume, the amount of ammonium salts and the amount of free ammonia present. Therefore, to get good results, these conditions must be the same when the copper from the sample is titrated as when the KCN is standardized. This is absolutely necessary.

Any nickel, silver or zinc present will also be titrated with the KCN, and so must be removed.

Process of Analysis.—Dissolve 1 gram of ore with 5 c.c. of HCl and 5 c.c. of HNO_3. Add 7 c.c. of H_2SO_4 and evaporate until the H_2SO_4 fumes copiously. Cool, add 30 c.c. of water and heat until all ferric salts are dissolved. Again cool and add 4 grams of pure granulated zinc and shake for five minutes. Heat until the zinc is all dissolved, then add 25 c.c. of H_2S water. Filter through a funnel, into the apex of which is stuffed a plug (made by shaking a mixture of equal amounts of glass wool and asbestos and then pouring in the funnel). Wash the precipitate copper until all zinc salts are removed, wash the copper back into the flask, place the flask under the funnel and pour through 10 c.c. of a hot 1:1 HNO_3 solution. Pour the same solution through several times, if necessary, to get all the copper dissolved. Finally, wash well to remove all the copper nitrate. Do not use more than 10 c.c. of HNO_3 (sp. gr. 1.10) in dissolving the copper.

Now boil to remove red fumes, dilute to 125 c.c. and, if silver is present, add a drop of HCl and filter off the AgCl. Add 10 c.c. of NH_4OH (sp. gr. 0.9) cool to room temperature and titrate.

Run in the standard cyanide solution *slowly* and with constant shaking until the blue color is almost gone.

The solution will now generally be turbid. Filter, wash once, dilute to 180 c.c. and carefully complete the titration by adding the cyanide drop by drop, shaking the solution after each drop until the blue tinge just disappears.

Standard Cyanide Solution.—Dissolve 21 grams of pure KCN and 2 grams of KOH in distilled water, dilute to 1 liter and mix

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[1] TREADWELL-HALL, "Analytical Chemistry," vol. 1, p. 172.

well. One cubic centimeter is equal to about 0.005 gram of copper. Now weigh accurately 0.2 gram of pure copper wire or foil and dissolve in a 250-c.c. Erlenmeyer flask with 10 c.c. of 1:1 HNO_3. Boil off the red fumes and dilute to 125 c.c. Add 10 c.c. of NH_4OH, cool to room temperature and titrate with the KCN solution *slowly* until the blue is nearly gone. Now dilute to 180 c.c. and carefully finish the titration until the blue just disappears.

Notes on the Process.—The zinc used to precipitate the copper must be all dissolved. This can be told by the cessation of the effervescence. If the solution becomes too concentrated, $ZnSO_4$ separates out and stops the solution.

If the H_2S causes a precipitation of copper sulfide, the filter should be washed with 5 c.c. of bromine water after the copper has been dissolved with HNO_3. This dissolves the sulfide.

If the titration is made rapidly, the blue color will persist even after enough HCN has been added to react with all the copper. This is because the reaction takes some time for completion. Hence, the titration must be made slowly.

A concentrated solution requires more cyanide for decoloration than a dilute one. A hot solution requires less than a cold one. The amount of cyanide required is affected by the amount of ammonia or ammonium salts present. Hence, the condition should be the same when the ore is titrated as when the cyanide is standardized.

The KCN solution keeps better when the KOH is added.

If only an approximate determination of the copper is desired, it can be made very rapidly by omitting the zinc precipitation. In this case treat 1 gram of the ore with 5 c.c. concentrated HNO_3, and boil till the copper is extracted and most of the acid driven off. Now add 5 c.c. more HNO_3, dilute to 125 c.c., add 10 c.c. of strong NH_4OH and run in the cyanide till the blue color is nearly discharged. Filter off and finish the titration as before. If there is a very large precipitate of $Fe(OH)_3$, repeat the process on a new sample of ore, adding nearly sufficient cyanide solution as calculated from the first determination before filtering.

SULFOCYANATE-PERMANGANATE METHOD FOR COPPER

As said on page 238, copper can be completely precipitated as CuCNS. When this precipitate is acted upon by a caustic alkali, the following reaction takes place: $CuCNS + NaOH = CuOH + NaCNS$. The $CuOH$ is left on the filter while the $NaCNS$ goes into solution. The sulfocyanic acid is titrated by a standard solution of permanganate, the final results of the oxidation being expressed thus:

$$5HCNS + 6KMnO_4 + 4H_2SO_4 = 3K_2SO_4 + 6MnSO_4 + 5HCN + 4H_2O.$$

That is, the sulfocyanic acid equivalent to 1 atom of copper requires 3 atoms of oxygen to oxidize it, which is the amount of oxygen required to oxidize 6 atoms of iron from divalent to trivalent condition. Then, to get the copper value of permanganate from the iron value, we make the following proportion: Cu : 6Fe : 63.57 : 335.04, or the iron value multiplied by 0.1897 gives the copper value of the permanganate.

When this titration is performed in acid solution, the reaction is not strictly in accord with the above written one and an empirical factor must be used, raising the calculated value for the permanganate by about 5 per cent. When the titration is made in an alkaline solution, as described below, the titration takes place in accord with the above reaction and the iron value of the permanganate used multiplied by 0.1897 gives the amount of copper present. No elements interfere.

Process of Analysis.—Place 1 gram or a sufficient amount of the ore (or metal) in a 200-c.c. beaker, add 5 c.c. of HCl and heat a few minutes, then add 10 c.c. of HNO_3 and heat until the ore is decomposed. Then add 10 c.c. of 1:1 H_2SO_4 and evaporate to fumes of SO_3. Add 50 c.c. of water containing 3 grams of tartaric acid and heat until all soluble salts are dissolved. Filter and wash, cool and add NH_4OH until the solution becomes alkaline (or becomes deep blue). Then add H_2SO_4 until the liquid is acid, and then 1½ c.c. more of strong acid (sp. gr. 1.84). Heat nearly to boiling and add 1 gram of Na_2SO_3 dissolved in water and then pour in slowly, and with vigorous stirring, 1 gram of KCNS dissolved in 20 c.c. of water. Allow the beaker to remain on the hot plate at a nearly boiling temperature for some time to allow any tartaric acid carried down by the precipitate to dissolve. This is important.

Now allow the solution to cool somewhat and filter, preferably through asbestos, and wash a half dozen times with warm water. Set a clean flask under the funnel (or wash out the suction flask if one is used) and pour over the white precipitate 30 c.c. of a hot 10 per cent solution of NaOH, and wash well with water.

Heat the filtrate to about 50° and run in, slowly at first and with constant stirring, standard permanganate solution. The liquid being titrated turns a green color. After an amount of permanganate has been added which, judging from the amount of the CuCNS which was obtained, is about half the amount necessary to finish the titration, test a drop for sulfocyanic acid by adding it on a white plate to a drop of ferric chloride strongly acid with HCl. If a deep-red color remains after stirring the drops, continue adding the permanganate, 5 c.c. at a time, until a test gives a slight red color, then test after every 2 c.c. until a test shows almost no red, indicating the absence of more than a trace of sulfocyanic acid ion. Now add 30 c.c. of 1:1 H_2SO_4, stir the solution until all MnO_2 dissolves and then finish the titration to the usual permanganate end color.

Notes on Process.—If the ore does not contain lead, it is not necessary to filter off the gangue. If it does, the lead sulfate must be filtered off, as it goes into solution in the ammonium tartrate and precipitates as lead sulfite with the CuCNS. Silver, if present in the ore, will precipitate as sulfocyanate but may be removed as AgCl with the lead.

The tartaric acid keeps antimony in solution. Not more than 3 grams should be used, as a crystalline compound of tartaric acid tends to separate from the solution when it cools, if too much is present. Hence, not too much should be used and the solution should be kept hot.

It is essential that the precipitation of CuCNS be made just as directed as to acidity, stirring and digestion after precipitation.

After a little experience it is easy to tell how much permanganate it is safe to add before testing for sulfocyanic acid. But it does no harm to begin testing from the first after each, say, 5 c.c. of permanganate. One can tell from the depth of the red color obtained on testing with ferric chloride when one is nearing the end. When the test gives almost no red, it will still require several cubic centimeters of permanganate to finish the titration when the solution is made acid. The permanganate used is one of which 1 c.c. equals 0.01 gram of iron or 0.001897 gram of copper.

The writer prefers to filter the CuCNS on an asbestos mat either in a Gooch crucible or in a funnel containing a plug of glass wool, on which the asbestos fiber is sucked down tightly. If the filtering is done through paper, the blank is increased. A blank should be made in any case to determine whether the NaOH contains oxidizable impurities. The blank should be almost nothing.

When the permanganate is added to the alkaline solution it turns green; on standing, MnO_2 separates, because the permanganate is reduced thus: $2KMnO_4 = K_2MnO_4 + 2O$. The oxygen oxidizes the sulfocyanate.

REFERENCE:

DEMOREST, *J. Ind. Eng. Chem.*, **5**, 215.

Note.—When the amount of copper in the ore is small, it is very satisfactory to dry and filter the washed CuCNS on a Gooch crucible and weigh as directed on page 155.

CHAPTER XXXV

ELECTROMETRIC TITRATIONS

In quite a few titrations the accuracy of analytical results is limited by indefiniteness of the end point. This indefiniteness may be due to the presence of material which itself has a color obscuring the color change of the titration, or to the presence of suspended solids, making the solution muddy, or the indicator used may not give a sharp change at the true end point. In many cases the end point can be more accurately detected by electrical means. This is particularly true when an outside indicator is necessary, as in the case of the dichromate titration of iron and the ferrocyanide titration of zinc.

The electrometric method of observing the end point of titrations may be used in any reaction when the end of the reaction is accompanied by an abrupt change in the potential between the solution which is being titrated and an electrode of constant potential, such as the calomel electrode. This abrupt change takes place when the hydrogen ions in an acid solution are completely neutralized by titration with an alkali or *vice versa*. In fact, the completeness of titration of very weak acids, the neutralization point of which is difficult to detect accurately with indicators, may be determined more satisfactorily by the electrometric end point. This is also true of oxidation and reduction reactions. The curve of potential between a solution containing an oxidizing reagent and a calomel electrode undergoes a sudden flexing when the oxidizing reagent is exactly reduced by a reducing reagent and *vice versa*. The change in conductivity may also be used in some cases.

Water is dissociated slightly, giving equal quantities of hydrogen and hydroxyl ions. The degree of dissociation is represented by the equation

$$(H^+)(OH^-) = 10^{-14}.$$

10^{-14} is the dissociation constant for water and means that 1 molecule of water out of every 10^{+14} is dissociated. The acid or hydrogen ion concentration of water is, therefore, 10^{-7}, and this represents exact neutrality, since water is exactly neutral because it has as many OH ions as H ions. Very few indicators have exactly this neutrality; indeed, most of the indicators used in acidimetry are decidedly acid and, therefore, do not give exact end points when some other acid is being titrated unless a correction factor is used (which is perfectly feasible). The acidity of rosolic acid is 10^{-7}, of phenolphthalein is 10^{-9} (it is therefore basic), of methyl orange is 10^{-4}. The electrometric end point method has the advantage of showing the exact end as well as being independent of the color or turbidity of the solution, and it also has the advantage that with it one can follow the change throughout the titration.

Theory of the Hydrogen Electrode.—If a bar of any metal is dipped into water, it will immediately give off some positive ions, and thereby become negatively charged. This charge will depend on the strength of the tendency of the metal to give off ions. For some metals a point will soon be reached at which the tendency for the ions in solution to deposit on the metal is as great as the reverse tendency. The potential attained is a measure of this tendency, for with the more metallic metals a relatively high concentration of ions can be built up with a correspondingly high potential. In any case, the potential attained will depend on two factors: the electrolytic solution pressure of the metal, and the osmotic pressure of the ions in the solution. If, now, two similar electrodes are dipped into two solutions of different concentration, and these solutions are electrically connected, the potential in the two cases will be different, and there will be a tendency for a current to flow from one electrode to another, if they are externally connected. The electrode which is immersed in the more concentrated solution will receive ions from the solution and will thus be positively charged, while the other electrode will tend to give positive ions to its weaker solution, and will be negatively charged, relative to the first electrode. Such a system, therefore, constitutes a battery, and a current can be obtained from it. The following is the formula for computing the potential difference which exists at the place of contact of a metal with a solution of its ions:

Let E = potential difference.
R = gas constant = volts × coulombs = 8,316 joules.
F = 1 faraday = 96,540 coulombs.
V = valence of the metal.
P = electrolytic solution pressure.
p = osmotic pressure.
T = absolute temperature.

Then $$E=\frac{RT}{VF}\log_e\frac{P}{p}$$

The total e.m.f. of a cell is the difference between the single potentials. Now the osmotic pressure is proportional to the concentration. Hence c can be placed for p. Then let C be substituted for P where C represents an ionic concentration which just balances the solution pressure and change to common logs by dividing by 0.4343:

$$E_{18^\circ}=\frac{0.058}{V}\log\frac{C}{c}.$$

This expression gives the voltage to be expected from a concentration cell of any material at 18°C.

The same principle can be applied to the case of hydrogen ions and a hydrogen electrode. Since the concentration of hydrogen gas in the electrode can be maintained constant, the potential will vary with the concentration of the ions in the solution, and may, therefore, be used as a measure of the latter and, thus, of the acidity or alkalinity of the solution. A hydrogen electrode is readily made by the use of a layer of platinum black or palladium black deposited on a platinum foil or wire and saturated with hydrogen gas at a definite pressure. The hydrogen gas is soluble in the platinum black, and attains a definite concentration for a given temperature and pressure. If this electrode is now dipped into a solution into which $c=1$, that is, in which there is a normal concentration of hydrogen ion, and if we then measure the potential difference between it and another similar electrode dipping into a solution of unknown hydrogen ion concentration, the solution being connected by a salt bridge (KCl), conditions are such that, if $V=1$ in both cases, the potential difference of the system $E=E_2-E_1$, or $E=0.058\log\frac{C}{C_2}-0.058\log\frac{C}{C_1}$, or $E=0.058\log\frac{C_1}{C_2}$. Since, in the first cell, hydrogen ion was taken as normal, $C_1=1$, and the equation becomes $E=0.058\log\frac{1}{c}$. This expression represents directly the change in potential of the cell with the change of the hydrogen ion concentration in the unknown solution.

In electrometric titration it is not convenient to use as a standard cell one composed of a hydrogen electrode dipping into a normal acid solution. It is more convenient to use the so-called calomel cell. This cell depends upon the equilibrium between the metallic mercury and the mercury ions in a saturated solution of mercurous chloride. The potential of the normal calomel cell is greater than the potential of the standard hydrogen cell by 0.285 volts. The calomel cell can, therefore, be used in place of the hydrogen cell if this allowance is made.

Oxidation and Reduction Potentials.—The advantages of the electrical method of titration in acidimetric reactions pertain equally well to that method of titration in oxidation and reduction reactions. While not so universally applicable to such reactions, the method is in cases even more convenient than in acid work, because the change in potential at the end point is more abrupt, so that it is seldom necessary to plot the readings on a coordinate scale. The apparatus used is practically the same as in acidimetric work.

Theory of the Method.—The change of valence which accompanies any reaction of oxidation or reduction is fundamentally the gain or loss of an election. Zinc going into solution in acid gains positive charges, *i.e.*, loses electrons.

$$\mathrm{Zn} - 2e = \mathrm{Zn}^{++}.$$

Ferrous ion, on changing to ferric, whether chemically by the action of chlorine or electrically by the electric current, also loses electrons.

$$\mathrm{Fe}^{++} - e = \mathrm{Fe}^{+++}$$

Both are oxidations. Chlorine reacting with hydrogen is reduced—it gains electrons. When permanganate is reduced to a managanous salt, the atom of manganese loses five positive valences, or gains five electrons—it is reduced. In general, oxidation is the loss of electrons; reduction is the gain of electrons.

The electric current is frequently used to effect both oxidation and reduction, the former at the cathode, where ions give up their electrons, and the latter at the anode, where the ions receive electrons from the circuit. Thus in a solution containing both ferrous and ferric ions, the former will be oxidized at the cathode and the latter reduced at the anode. If no external e.m.f. is applied and a single platinum wire is inserted into such a solution, the wire will acquire a positive or a negative potential, depending on the relative concentrations of the ferrous and ferric ions, the former tending to give electrons to it, thus charging it negatively, and the latter having the reverse tendency. That such a potential exists can be shown by connecting two beakers containing solutions of different concentrations of ferrous and ferric ions by means of a "salt bridge," and inserting into each beaker a platinum wire. If the two wires are now joined, a current will flow, for the tendency for the ferrous ions to give up electrons will be relatively the greater in one beaker, and the tendency for the ferric ions to take up electrons from the wire will be the greater in the other. The system constitutes a cell, therefore, the potential of which can be measured. If the relative concentration of ferrous and ferric ions in one solution were known and unchanged, the potential would be a measure of the relative concentrations in the other. This is experimentally not realizable, however. Instead of using such a system, a single ferrous-ferric solution is connected with a normal calomel electrode as a standard. The potential of this cell is based on a standard, and is a reliable index of concentrations.

The potential of such a cell is given by the formula:

$$E = A + \frac{RT}{VF} \log_e \frac{(\mathrm{Fe}^{++})}{(\mathrm{Fe}^{+++})},$$

in which the symbols have their usual significance. Substituting numerical values and changing to common logarithms,

$$E = A + 0.058 \log \frac{(\mathrm{Fe}^{++})}{(\mathrm{Fe}^{+++})}.$$

A is a constant which can be evaluated in an experimental case in which the ratio $\frac{(\mathrm{Fe}^{++})}{(\mathrm{Fe}^{+++})}$ is equal to 1, when the second term becomes zero. This is, of course, when ferrous and ferric ions are present in equal quantities. The value thus determined is 0.047. The potential of such a system may thus be used as a measure of the relative concentrations of ferrous and ferric ions. Obviously, when the relative concentrations are changing, as in the course of a titration, there will be a slow change in voltage corresponding to the addition of oxidizing or of reducing agents. It is, however, only when one of the two ionic concentrations becomes very small as compared with the other that there will be any large change in voltage. Actually, the change may be almost imperceptible until the end point is reached, and will then be very large and abrupt, as shown in Fig. 12.

The apparatus used is shown diagrammatically in Fig. 13. The battery *B* is a dry cell connected through a key to the sliding contact rheostat *R*. When the key is closed, a small current flows continually through this rheostat. By means of the sliding contact, a variable potential may be drawn off from this main circuit, this being continuously and directly measured on the voltmeter *V*. Another branch circuit contains the beaker of solution to be titrated, with the electrodes immersed and connected through a sensitive galvanometer *G*, and a spring contact key. This system serves as a battery, as explained above and gives rise to a potential. The method of operation is simply to slide the contact key on the rheostat until the voltage drawn from the dry battery is equal to that produced by the solution being measured. This will be shown by the fact that no current passes through the galvanometer when the spring contact key is pressed down. When this point is reached, the potential of the cell will be indicated directly by the voltmeter, and since the relation between voltage and hydrogen ion concentration is known, the values may be read directly on the voltmeter as soon as the point of balance is found. If the entire course of a titration is to be followed, readings may be recorded for each addition of alkali in the titration. If, as is more usual, only the acid titer is desired, the titration is continued until the point is reached which corresponds to the end point of the particular reaction used and the volume of alkali is recorded as in an ordinary titration. In this case the rheostat may be set at once to give the proper reading and the titration continued until the galvanometer shows no current. It is important, whenever a balance has not yet been reached, to *close the spring contact key only momentarily by a slight tap.* Otherwise, current is drawn from the system and the hydrogen electrode may become discharged.

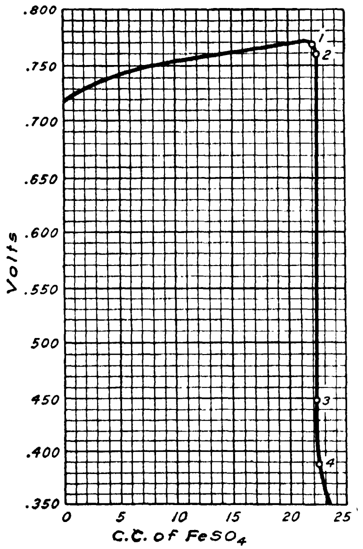

FIG. 12.

The apparatus used for oxidation and reduction reactions is the same as for hydrogen electrode titrations, with the following exceptions:

The hydrogen electrode should not be coated with platinum black, but should, on the contrary, be carefully burnished, so as to expose the minimum possible surface. The larger foil electrodes sometimes used for acidimetric work cannot be used for oxidation potentials. The electrodes must be kept clean, and should be occasionally treated with hot concentrated chromic acid.

For ordinary titrations, the voltmeter is not necessary, but is desirable in order to follow the course of the titration. In acidimetry the calomel cell is connected to the positive side of the main circuit, but in oxidimetry this is reversed.

The Calomel Electrode.—To fill the calomel cell:

1. Place about 3 c.c. of pure mercury in the bottom of the carefully cleaned cell.

2. Above this place a layer, about 5 mm. thick, of a mercury-calomel paste, made by rubbing together in a mortar mercurous chloride (calomel) and a little mercury, the whole moistened with a few drops of normal potassium chloride solution.

3. Prepare a liter of accurately normal potassium chloride solution and saturate it with calomel by shaking, allowing to stand and then decanting from the remaining calomel.

4. Fill the calomel cell to within a ½ in. of the top with this solution. Close the cell by inserting the ground-glass stopper tightly. Establish

permanent connection between the upper side arm of the cell outlet and the outlet of the KCl reservoir.

5. Just before use, allow a little of the KCl solution to run through the cell, opening both the stop-cock and the pinch-cock for the purpose until the side tube has been well washed and is filled with fresh KCl solution. Close the pinch-cock, insert the side tube of the cell in the titration beaker and close the ground stop-cock lightly. This prevents undue diffusion of the solutions, yet allows sufficient conductance of electricity for the potential measurement. After, perhaps, a dozen titrations, or after standing for two or three hours in contact with titrating solutions, enough diffusion will have taken place so that a little KCl solution should again be run through the side arm. For exact work this needs to be done more often.

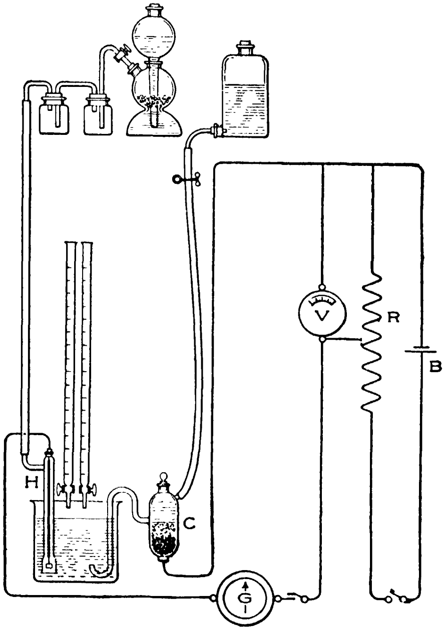

Fig. 13.

To Titrate Any Simple Acid or Alkali.—Run a known volume of the solution to be titrated into the titration beaker. Insert the electrodes connected as directed above. Add alkali or acid until near the end point. The first additions of reagent will cause relatively little change in potential, due to the large excess of the original solution present, but as the neutrality point is reached, each addition of reagent causes a correspondingly larger change of potential until at exact neutralization there is a sudden large jump. For titrations in which an accuracy of 5 per cent is sufficient, the occurrence of this sudden change may be taken as the end point. When a greater accuracy is desired, the potential corresponding to the exact equivalence point must first be determined. This can be done once for each reaction in either of two ways. A solution of the salt formed in the titration may be made up of about the same concentration as is produced by the titration, *i.e.*, of potassium oxalate for the titration of oxalic acid with potassium hydroxide, of ammonium chloride for the titration of hydrochloric acid with ammonia, etc. The potential indicated by this salt solution is the one at which the corresponding titration is complete. Once this is done, the process of titration consists simply in adding either reagent until this potential is indicated. If this method is not possible or convenient, a preliminary titration must be made in which the readings for each addition of alkali or acid are recorded and the two values are plotted against each other.

Determination of Ferrous and Ferric Iron in One Sample.—The solution is first reduced with stannous chloride solution, as in the titration for ferric iron alone. The volume gives the amount of ferric iron. A slight excess of stannous chloride is then added, and the titration continued with standardized dichromate solution. The first marked increase in voltage corresponds to the oxidation of the excess of stannous chloride, and is the point at which the second part of the titration begins. The volume of dichromate required to pass from this point to a second sharp increase in voltage is the volume required to oxidize all the iron present from ferrous to ferric, and, therefore, is a measure of the total iron present. In this one titration, therefore, both ferrous and ferric iron may be determined. The method is applicable to many raw materials, such as iron ore, sand, barium carbonate, zinc and lead oxide. These substances do not interfere, but the presence of nitric acid always makes the titration impossible. If nitric acid is required for solution of the raw material, the iron must first be precipitated as hydroxide and dissolved in hydrochloric acid. Manganous manganese and titanium also are not affected by stannous chloride, but vanadium is, and must be separately determined if it is present.

The Determination of Vanadium and Chromium in Ferro-vanadium.—Dissolve 3 grams of the sample in 75 c.c. of nitric acid (sp. gr. 1.13). When the solution is almost complete, add 10 c.c. of HCl to assist in decomposing carbides. After the volume has been reduced about one-half, add a few drops of hydrofluoric acid to remove silica. Then add 50 c.c. of sulfuric acid and evaporate until fumes of sulfuric acid appear, with the object of removing all hydrochloric acid. Dilute in a standardized flask with water to 1 liter. With a standardized pipette remove two 100-c.c. portions.

To 100 c.c., add 20 c.c. sulfuric acid and water to make 300 c.c. Boil and add silver nitrate and ammonium persulfate to oxidize chromium, vanadium and manganese (see page 131). After 10 minutes' boiling, add 3 c.c. 1:3 hydrochloric acid to decompose permanganic acid. Boil 10 minutes longer, cool, add 25 c.c. sulfuric acid and titrate at 5°C. with a ferrous sulfate solution equivalent to dichromate solution containing 0.001 gram Cr per cubic centimeter. The titration includes chromium and vanadium.

To a second 100-c.c. portion add a few cubic centimeters of ferrous sulfate solution to reduce any chromium existing in the oxidized condition and follow this with 20 c.c. of sulfuric acid and 40 c.c. of nitric acid, together with water enough to give a volume of 200 c.c. Evaporate by boiling quietly at such a rate that in one hour the volume is reduced to 100 c.c. Under these conditions 99.5 per cent of the vanadium is oxidized. Cool to 5°C. and titrate with ferrous sulfate. To calculate, divide by 0.995 and by 3 and multiply by 2.943. This gives the percentage of vanadium.

The percentage of chromium may be calculated by subtracting the per cent obtained by the second oxidation from that obtained by the first and dividing the difference by 2.943.

Notes and Precautions.—In oxidizing with ammonium persulfate and silver nitrate it is important to have the sulfuric acid and water in the proportions given. After adding the ammonium persulfate and after adding the hydrochloric acid, the solution should be boiled at least 10 minutes.

The concentration of nitric acid, the initial and final volumes and the rate of evaporation are important steps in securing a regular oxidation of vanadium by nitric acid.

Any insoluble matter in the ferrovanadium suspected of containing vanadium should be fused with sodium peroxide. After leaching, boil the alkaline solution for 20 minutes. Then acidify with sulfuric acid and add to the main portion of the solution before making up to volume. It is rare that this treatment is necessary.

If a solution containing 2.883 grams of potassium dichromate in 1 liter should be used, each cubic centimeter should correspond to 1 per cent of vanadium when a sample weighing 0.3 gram is used.

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CHAPTER XXXVI

THE ANALYSIS OF COAL AND COKE

Coal is a mixture of partially decomposed and carbonized organic matter resulting from swamp vegetation, usually of the Carboniferous Age, mixed with all kinds of inorganic mineral detritus washed into the swamp waters. This inorganic mineral material is very similar to clays, running all the way from nearly pure fire clay to very impure, and sometimes containing considerable amounts of quartz and calcium carbonate. Pyrite is a very common constituent. It will be seen, therefore, that coal is a very complex substance. Coal does not contain gas except in minute quantities, but when the coal is heated, the organic materials of the coal are decomposed, resulting in the production of gases, liquids and solids. The liquids make chiefly a complex mixture known as tar.

In the laboratory examination of coal the points to be investigated are usually: First, the amount of moisture which it contains as it occurs in the mine or on the market. Second, the amount of the impurities present that affect its use, such as ash, sulfur and phosphorus. Third, the amount and quality of the coke which it will produce. Fourth, the improvement which it undergoes by "washing." Fifth, the fuel value, including the calorific power and the evaporating power. Sixth, the proximate composition, to indicate the nature of the coal and its probable field of usefulness.

The sampling of coal is always a matter of considerable difficulty, as it deals with a mechanical mixture of several minerals which differ greatly in specific gravity; namely, pure coal, slate, bone coal and iron pyrite. These constituent minerals may occur in all degrees of size; for instance, the pyrite may be present as barely visible grains scattered all through the coal or as large lumps and streaks. It is obvious that in the latter case the difficulty of securing a small sample which shall contain the same percentage of the heavy pyrite as does the mass from which it is drawn is formidable (see page 2).

Finely crushed coal is liable to oxidation and change of composition on standing exposed to air at ordinary temperatures. Hence, the analysis should be made soon after the final sampling.

The laboratory processes in use for coal testing comprise the "proximate" analysis, the ultimate analysis, the determination of sulfur and phosphorus, tests of the coking power, washing the coal and, finally, the determination of the heating power either by calculation from the results of the ultimate analysis, or by use of the calorimeter.

PROXIMATE ANALYSIS

The method for proximate analysis here used is as given by Prof. E. E. Somermeier of the Department of Metallurgy, Ohio State University, in his book, "Coal."

This analysis gives the composition of the coal under four headings as follows: moisture, volatile matter, fixed carbon and ash.

The results obtained are more or less dependent upon the exact process used and small variations in working out the details of the process may make a considerable difference in the results actually obtained, while a distinctly different process gives radically different values for some of the determinations. Hence, the results are relative and not absolute and should be so regarded both by the chemist and by the user of the coal.

Moisture.—The term "moisture" includes only the more or less loosely held water which is driven off by heating 1 gram of the finely ground sample for one hour at 105°C. A finely ground sample of coal during the operation undergoes changes due to oxidation and escape of gases, hence the actual value obtained for moisture is the amount of water driven off plus or minus any oxidation changes. In most coals, if not ground excessively fine, these oxidation changes are of minor importance compared to the moisture loss, so that the reporting of this net loss as moisture does not lead to any serious errors, although it practically never represents the exact amount of water expelled. A sample of coal which has been heated for one hour at 105° will give off more moisture and undergo further oxidation changes if heated to a still higher temperature, the amount of moisture given off depending upon the kind of coal and upon the increase in temperature. The extent of the oxidation also increases with the temperature and varies with the kind of coal and fineness of the sample. While it is true that the results for moisture obtained by heating the sample to 105° have no absolute value, but merely a relative one, it is equally true that, when two samples of approximately the same kind of coal are treated in the same way for moisture by heating to 105°, the difference in the results obtained show very closely the difference in the amount of loosely held moisture in the coal. Usually this is what the user of the coal wishes to know and on this account the moisture determination has importance and value.

Volatile Matter.—The determination of volatile matter is an arbitrary one and the results are obtained by following a certain prescribed procedure, which is, essentially, to heat 1 gram of the finely ground sample in a covered platinum crucible over the full flame of a Meker burner for seven minutes. The loss in weight represents moisture plus volatile matter. Subtracting the value for moisture from this result gives the amount of volatile matter in the coal.

This determination cannot be regarded as entirely satisfactory, as the result obtained is to a considerable degree dependent upon the particular conditions under which the sample was run and two different chemists in two different laboratories, both trying to follow out the same method of procedure, may easily obtain results for volatile matter upon the same sample of coal which may differ by 2 or 3 per cent. Furthermore, some high-moisture coals suffer mechanical losses during the heating to drive off the volatile matter. Such samples require special treatment to insure results of even approximate accuracy. On account of such possible differences and errors, this determination cannot be regarded as very exact. It is, however, true that the same chemist working in the same way with the same crucibles, the same height of gas flame, the same burner, etc., can obtain results which will duplicate within a few tenths of 1 per cent, and in control work the same chemist's results on approximately the same coals ought to be comparable among themselves to within less than 1 per cent. The amount of volatile matter in itself gives very little idea of the coal, as two coals with approximately the same amount of volatile matter may differ very greatly in heating value, physical properties, etc., and any significance which the determination of volatile matter actually has is largely a relative one, which may be of value when the same or similar coals are compared with one another.

The volatile matter consists essentially of any combined water in the coal plus a portion of the sulfur, on an average probably about one-half of the total sulfur present in the coal, plus the nitrogen in the coal, plus hydrocarbons of unknown and varying composition. The nitrogen and combined water in the volatile matter have no heating value and, if present in large amounts, the heating value of the combustible will be correspondnigly lower.

Fixed Carbon.—Fixed carbon represents the difference obtained by subtracting the percentage of moisture, volatile matter and ash from 100. The fixed carbon, as its name indicates, is mostly carbon. Approximately one-half the sulfur in the coal present in the form of pyrite and a variable portion of that present as organic sulfur remains with the fixed carbon and the heating value of the fixed carbon is, on this account, somewhat lower than that of pure carbon. On the other hand, small amounts of hydrogen may be retained in the fixed carbon which would slightly increase its heating value. In most coals the heating value per unit of the fixed carbon is not far from that of carbon —8,100 cal.—and this value may be used in estimating heat values without any great error. With high sulfur coals, a somewhat lower value, approximately 30 cal. lower for each per cent of sulfur in the coal, is probably more nearly a correct value. This is based on the assumption that one-half of the sulfur remains with the fixed carbon and that not more than traces of hydrogen are retained in the fixed carbon.

Ash.—As ordinarily reported, this is the weight of ignited inorganic mineral matter in the coal. It is not the same as the inorganic mineral matter of the coal, for clay loses water on heating, sulfides are oxidized and carbonates are calcined.

METHODS OF ANALYSIS

The samples from the sampling room or laboratory should be sent to the chemical laboratory in wide-mouth bottles securely closed with rubber stoppers. Ordinary 4-oz. wide-mouth bottles are very convenient for coal samples.

Weighing Out a Sample for a Determination.—In weighing out portions of the laboratory sample for a determination, the sample should be well mixed. An efficient method of mixing is as follows: The material is thoroughly mixed by giving the bottle 15 to 20 rotations with an up-ending and tilting movement of the bottle to insure mixing of the top and bottom portions of the sample. For satisfactory mixing in this way the sample should not fill the bottle more than half full. After the mixing in the bottle, the stopper is removed and the sample still further mixed by means of a sampling spoon, and successive small portions taken until the amount required for the determination is secured, especial care being taken to securely stopper the bottle again before setting it aside for other determinations. If the sample more than half fills the bottle it should be emptied out on paper, well mixed and a sufficient amount discarded until the remainder is small enough to be handled properly in the sampling bottle.

Moisture.—A 1-gram portion of the well-mixed 60-mesh sample is *quickly* weighed into an empty capsule or crucible and heated for an hour at 105°C. in a constant-temperature oven, previously brought to the temperature. The capsule is then removed from the oven, *quickly* covered and cooled in a desiccator over sulfuric acid.

The loss in weight times 100 is considered as the percentage of moisture. The writer prefers, for moisture determinations, porcelain capsules about 1 in. high by 1⅝ in. in diameter at the top. They are much more substantial and satisfactory than the ordinary porcelain crucible.

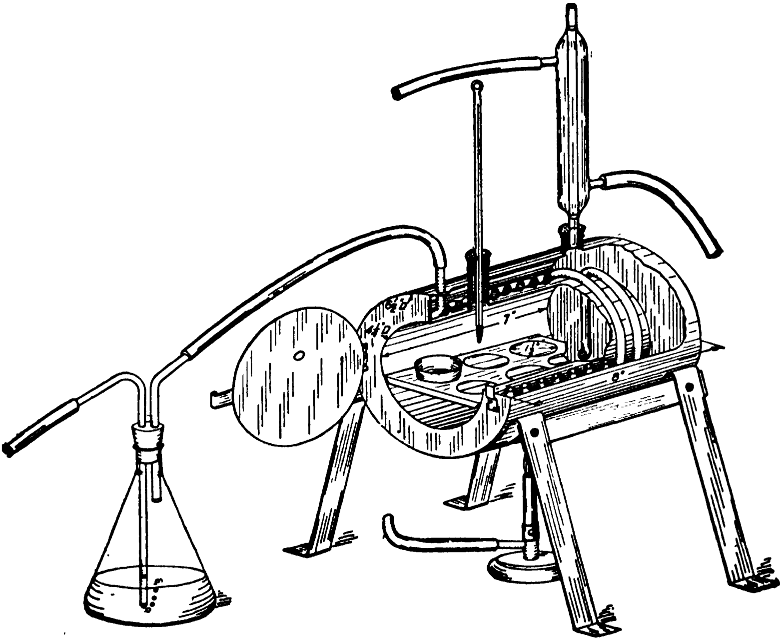

FIG. 14.

The lids used in connection with the capsules are stamped from sheet aluminium. They are light and unbreakable and much more convenient to handle than the ordinary covers used with porcelain crucibles. In weighing out the sample at the beginning of the determination the lid is placed upon the balance pan under the empty capsule in which the sample is weighed.

The oven used for a number of years in this laboratory is a double-walled copper cylinder, see Fig. 14; the space between the outer and inner walls being filled with a solution of glycerine in water, the proportions being so adjusted that the boiling solution maintains a temperature of 105°C. in the inner chamber of the oven. The inner cylinder is 4½ in. in diameter by 7 in. long. A removable perforated shelf fits into this inner cylinder, the perforations holding six capsules. The outer cylinder is 6½ in. in diameter by 8 in. long. Concentration of the solution is prevented by means of a condenser fitted onto the top of the outer cylinder. Air is admitted into the inner chamber of the oven through a coil of block tin or copper tubing, which passes around the inner cylinder and is surrounded by the glycerine solution. The inner end of this tubing is soldered into the rear wall of the inner chamber; the outer end is connected to a flask containing concentrated sulfuric acid. During a determination a current of air, dried by passing through the sulfuric acid, is passed through the copper or tin tube into the inner chamber of the oven. Passing over the samples, it takes up the moisture and escapes through a small opening in the top of the door of the oven. The air is passed through at such a rate that a volume equal to the capacity of the oven passes through every six or eight minutes. Operating a moisture oven in this way insures a uniform condition in the oven irrespective of laboratory humidity and temperature conditions, and results run at different times are strictly comparable, which is not the case in an ordinary moisture oven.

The cut shows nine turns of tubing; however, four or five turns are probably just as efficient and are less expensive.

The use of sulfuric acid in the desiccator in which the moisture sample is cooled gives more concordant results than where calcium chloride is used. Experiments show that if the dry sample is allowed to remain over calcium chloride for any considerable period of time, it increases in weight and the results for moisture are accordingly low. To avoid the danger of sulfuric acid, in the desiccator, splashing up on the bottom of the capsule when the desiccator is carried around the laboratory, a thin sheet of asbestos paper should be placed below the capsule, care being taken to have it fit loosely enough in the desiccator to allow free circulation of air.

Ash.—The ash is determined in the residue of coal from the moisture determination. The capsule containing the coal is placed in a muffle furnace and slowly heated until the volatile matter is given off. This slow heating avoids coking the sample and renders it easier to burn to ash. After the volatile matter is expelled, the temperature of the muffle is raised to redness (750° C.) and the heating is continued until all black carbon is burned out. The capsule is then removed from the muffle furnace, cooled in a desiccator and weighed. It is then replaced in the muffle, for 30 minutes, again cooled and reweighed. If the change in weight is less than 0.0005 gram, the ash is considered burned to constant weight. If the variation is greater than this, the ash is again ignited for 30 minutes and again cooled and reweighed, the process being continued until the difference in weight between two successive ignitions is less than 0.0005 gram. In the case of coals high in iron, ignition to constant weight is sometimes difficult on account of small variations in weight due to oxidation and reduction of the compounds of iron. The amount of ash as determined represents the ignited mineral matter in the coal.

In regular routine work the cooling in desiccators may be dispensed with and the capsules cooled on clay triangles in the open air. A set of six triangles mounted on a wood base is very convenient for carrying the capsules from the furnace to the balance and from the balance back to the furnace. This arrangement is lighter and easier to handle than desiccators and the time required for cooling is much less.

The capsules cooled in air weigh about 0.0005 gram more than if cooled in desiccators, hence the ash results run a trifle high; but for most samples the difference is of very minor importance and the saving in time and labor considerable. If results of highest accuracy are required, the cooling should be done in desiccators.

Volatile Matter.—A 1-gram sample of the fine (60-mesh) coal is weighed into a bright, well-burnished 20-gram platinum crucible with a close-fitting cover. The crucible and contents are heated upon a platinum or nichrome triangle for seven minutes over a Meker flame not less than 15 cm. high. The crucible bottom should be ¾ in. from the top of the burner.

The crucible and residue are cooled and weighed, the loss in weight minus the weight of the moisture in the sample determined at 105°C., times 100, equals the percentage of volatile matter.

To protect the crucible from air currents it is desirable to enclose the flame in a chimney. A cylindrical chimney 15 cm. long by 7 cm. in diameter, notched at the top so that the platinum triangle is about 3 cm. below the top of the chimney, makes a satisfactory working arrangement.

This chimney is preferably of sheet iron lined with asbestos, but a fairly satisfactory chimney can be made by moistening a thick sheet of asbestos and rolling it into a cylinder. This, if well wrapped with wire, makes a fairly serviceable chimney.

For lignites and coals containing a high percentage of moisture, the method should be modified by giving the sample a preliminary heating

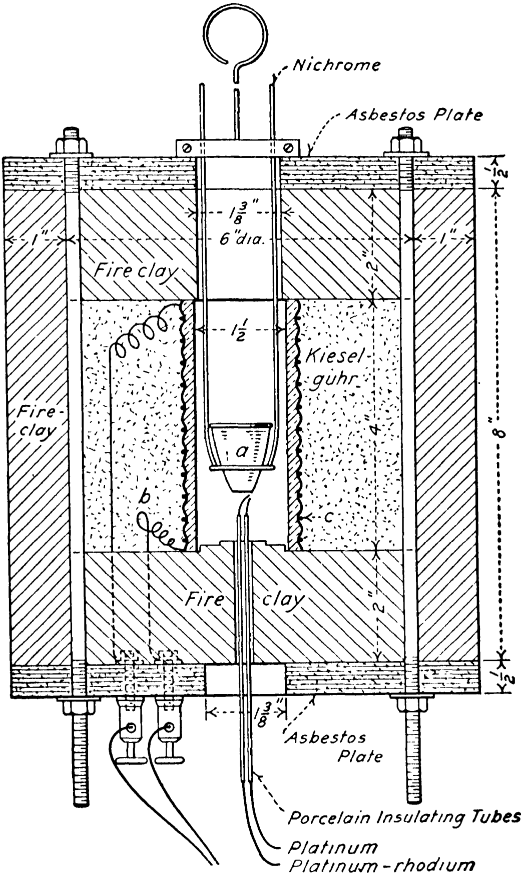

FIG. 15.

at a low temperature for several minutes to drive out the moisture, in order to avoid mechanical losses which will occur if such a sample is heated over the full flame of the burner from the beginning. This preliminary heating for three to four minutes should be followed by the regular seven-minute application of the full flame, after which the sample is cooled and weighed as in the regular determination.

The higher the temperature at which the volatile matter is expelled the greater is the percentage of volatile matter obtained. The latest data on this subject (Sept., 1912) is by Fieldner and Hall.[1] As a result of their experiments they recommend 950°C. as the most desirable temperature at which to make this determination. Their results using a No. 4 Meker burner with natural gas compare very favorably with their results obtained by heating the sample in an electric furnace. The crucible should be at least hot enough to melt pure K_2CrO_4 (melting point 940°C.).

Use of a Vertical Electric Tube Furnace; or a Gas or Electrically Heated Muffle Furnace.—The furnace may be of the form as shown in Fig. 15. It is to be regulated to maintain a temperature of 950°C. (±20°C.) in the crucible, as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal is bought, a Meker burner may be used.

Weigh 1 gram of the coal in a weighed 10- to 20-c.c. platinum crucible, close with a capsule cover and place on the platinum or nichrome wire supports in the furnace chamber, which must be at a temperature of 950°C. (±20°C.). After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, tap the cover lightly to seal the crucible more perfectly and thus guard against the admission of air. After heating exactly seven minutes, remove the crucible from the furnace and, without disturbing the cover, allow it to cool. Weigh as soon as cold. The loss of weight minus moisture equals the volatile matter.

Modification for Subbituminous Coal, Lignite and Peat.—Mechanical losses are incurred on suddenly heating peat, subbituminous coal and lignite; therefore, they must be subjected to a preliminary gradual heating for five minutes; this is best done by playing the flame of a burner upon the bottom of the crucible in such a manner as to bring about the discharge of volatile matter at a rate not sufficient to cause sparking. After the preliminary heating, transfer the crucible to the volatile-matter furnace and heat for six minutes at 950°C. as in the regular method.

The permissible differences in duplicate determinations are as follows:

	Same Analyst, Per Cent	Different Analysts, Per Cent
Bituminous coals..........	0.5	1.0
Lignites..................	1.0	2.0

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[1] Eighth International Congress of applied Chemistry, **10**, 139.

Notes.—The cover should fit closely enough so that the carbon deposit from bituminous and lignite coals does not burn away from the under side.

Regulation of temperature to within the prescribed limits is important.

Fixed Carbon.—The fixed carbon is the difference between 100 and the sum of the moisture, ash and volatile matter.

The Determination of Sulfur in Coal. Eschka's Method.—Sulfur exists in coal in three forms: pyrite, "organic sulfur" and sulfates. By heating coal with a mixture of MgO and Na_2CO_3, and with ample access of air, all unoxidized sulfur is converted to sulfites and sulfates of soda and magnesia. On boiling the burned mass with water, these, as well as any sulfuric acid existing previously in the coal as sulfate, are all dissolved out as alkaline salts. By adding bromine water to the solution, the sulfites are oxidized to sulfates, and then the total sulfur can be estimated as $BaSO_4$, by precipitation with $BaCl_2$.

Preparation of the Soda-magnesia Mixture (Eschka Mixture).—Procure a "light" calcined magnesium oxide, which must be free from sulfur and water. If it contains moisture, ignite it at a dull red-heat in a covered platinum crucible. The heavy, dense oxide is not satisfactory.

Mix two parts of the MgO with one part by weight of pure Na_2CO_3 previously dried at a dull red-heat. Grind the two together until thoroughly mixed, and keep the mixture in a glass-stoppered bottle.

If a satisfactory sample of sulfur-free MgO is not available, it may be prepared as follows:

Take a good quality of commercial "light calcined magnesia"; add about 2 per cent of c.p. sodium carbonate and then stir it up in enough boiling water to make a thin liquid. Boil the mixture a few minutes and let settle; decant off the liquid by a siphon. Add water, stir up, settle and again decant. Continue this washing by decantation until a portion of the liquid, after being acidified with HCl, shows no trace of sulfates when tested with $BaCl_2$. Now pour the MgO onto a large filter, let it drain and air dry. It is now free from sulfur compounds. Ignite the air-dried MgO in a covered platinum crucible until all water is expelled.

A clean tin bucket can be used in this process where a quantity is to be prepared.

Process of Analysis.—Weigh 1 gram of the coal or coke (which must be finely powdered, especially in the case of coke), then weigh or measure out roughly 3 grams of the "Eschka mixture." Put about two-thirds of this into a 30-c.c. platinum crucible.

Add the weighed coal and stir the mixture in the crucible thoroughly with a small platinum spatula or glass rod, and then settle it down by tapping the crucible on the table. Now cover the contents of the crucible with the remaining portion of the "Eschka mixture." Set the crucible, in an inclined position, over a small alcohol or sulfur-free natural-gas flame, so that the tip of the flame may barely touch the crucible near the *top of the mixture*. The heat must be carefully regulated, so that no blackening of the white cover layer takes place, and no trace of smoke appears. The cover should be laid against the mouth of the crucible to assist the draft. The mixture soon ignites and will gradually burn through, as may be observed through fissures which open in the mass. The coal will usually burn completely in less than an hour. The heat may be raised toward the end of the combustion and the lamp set back under the bottom of the crucible. A higher heat may be used with cokes from the start; as these give no volatile products and burn slowly. Stir up the powder occasionally with a hot glass rod or platinum wire. When the burning is complete, all trace of the black coal will have disappeared and only a light, reddish-gray mass remain. Cool and then pour the powder into a 200-c.c. beaker. Add about 75 c.c. of boiling water, stir and digest on a water-bath. Then filter, washing the residue twice by adding about 30 c.c. of hot water, and decanting off, then transfer to the filter. Wash on the filter until the volume of the filtrate amounts to about 200 c.c. This will extract practically all of the sulfur.

Add bromine water to the filtrate until the liquid is colored yellow; then add 3 c.c. of HCl and warm until the CO_2 is expelled. Test the solution with methyl orange to make sure that it is distinctly acid. Heat to boiling and slowly, and with constant stirring, add 10 c.c. of $BaCl_2$ solution (10 per cent). Set the beaker on a warm plate, but do not let it come to boiling. Stir the liquid occasionally until the $BaSO_4$ becomes granular and settles well. Now filter, wash, dry, ignite and weigh the $BaSO_4$. Calculate the sulfur as S.

Always examine the *residue* which was extracted with water, by washing it off the filter into a beaker, and then adding a little HCl and warming. All will dissolve but a little ash. If more than a trace of *unburned* coal is seen in the residue, the analysis must be repeated.

The residue sometimes retains a very small trace of sulfur. To test it, add a little bromine water with the HCl as above and boil. Filter off the liquid and add $BaCl_2$. If any sulfur is found, add it to the main precipitate.

Notes on the Process.—This is one of the best methods for the determination of sulfur in coals. If care be taken in all details, especially as to rate of heating, there is no loss of sulfur whatever.

It has been proposed to substitute K_2CO_3 for the Na_2CO_3, the claim being made that there is less danger of loss of S with the potassium carbonate, but experience has shown it to be absolutely unnecessary.

The use of alcohol or sulfur-free natural gas as a source of heat is *essential.* All coal gas contains sufficient sulfur to *vitiate* the results.

The most difficult step in the process is the burning out. In analyzing coke, much time can be saved by using a higher heat than is given by an alcohol lamp. This can be obtained by using a gasoline blast lamp or working in a muffle heated by gasoline. If the muffle is heated by coke or coal gas, care must be taken that no sulfur gets into it from the fuel.

Determinations of ash in coal and coke must not be made in the muffle at the same time with sulfur determinations; as the SO_2 formed will be absorbed by the Eschka mixture and make the results high.

Cokes can be burned with Eschka mixture in a platinum dish. They should be stirred frequently, which will hasten the combustion. It is unsafe to treat coals high in volatile matter in this way, because the gas given off must be burned in the mixture and not on the surface, or sulfur may escape. They must be burned in the crucible, and by properly regulating the air supply and the temperature the gas can be rapidly burned as it is given off. When the volatile matter is expelled, the heat can be raised and the mixture stirred.

A blank determination must be run on the reagents. It is best made by adding a known amount of sulfur as sulfate to the extract from a blank Eschka mixture which has been put through the usual procedure.

Sulfur in the Calorimeter Washings.—The determination of the sulfur in the washings from the calorimeter is as follows: The washings are slightly acidulated with hydrochloric acid and filtered from the residue of ash, the filtrate is heated to boiling and the sulfur precipitated as in the Eschka method. Register has shown that, if 5 per cent of nitrogen is present in the gases in the bomb calorimeter, the sulfur in the coal is almost completely oxidized to H_2SO_4 (see *J. Ind. Eng. Chem.*, **6**, 812).

REFERENCES:
ESCHKA, *Z. anal. Chem.*, **13**, 344.
DROWN, *Trans.* Am. Inst. Min Eng., **9**, 660.

The Determination of Phosphorus in Coal and Coke.—Ten grams of the coal are carefully burned to ash in a porcelain crucible. The ash is then analyzed for phosphorus exactly as though it were an iron ore, except that it is always necessary to fuse the insoluble portion. HCl will not dissolve all the phosphorus out of the ash, even on prolonged boiling, though the amount left is usually very trifling.

Process of Analysis.—Mix the ash from 10 grams of the coal with six times its weight of pure Na_2CO_3 and half its weight of $NaNO_3$. Fuse the mixture in a platinum crucible, soften the fusion with water, dissolve in an excess of HCl, evaporate to dryness, take up with HCl and water and filter from the SiO_2; then proceed as by the yellow precipitate method for phosphorus in iron ores (page 49 *et seq.*).

The fusion can be avoided by the use of hydrofluoric acid as follows: Add 5 c.c. of dilute HCl and 10 c.c. of HF to the ash in the platinum crucible. Evaporate to dryness in a good hood; do not bake the residue and thus render it insoluble. When cool, add 15 c.c. of dilute HCl and heat. The residue should dissolve completely, but a little insoluble matter may be filtered off and neglected. Put the solution into a flask, add NH_4OH, then HNO_3, then molybdic acid solution and "shake down" the phosphorus as in the Emmerton method. The yellow precipitate may be either weighed or titrated.

REFERENCE:
CAMP, J. M., *Iron Age*, **65**, 17; "Methods around Pittsburgh," p. 139.

THE ULTIMATE ANALYSIS OF COAL

The Determination of the Carbon and Hydrogen by Combustion in Oxygen.—The coal, placed in a boat of porcelain or platinum, is burned in a combustion tube, through which a current of purified air and oxygen is passed. The H_2O and CO_2 produced are absorbed and weighed. As the coal contains sulfur, the gases produced by the combustion must be passed over lead chromate to absorb the SO_2 formed.

The same chromate can be used for many determinations. As long as it does not turn green for more than one-fifth of the length in the tube, it is perfectly safe. The writer has used the same chromate for over fifty combustions, and then tested it by burning sulfur in the tube, and found no SO_2 escaping the chromate.

The principal difficulty in the process arises from the fact that coal begins to decompose at a low temperature, giving off, among other products, methane, a gas which it is very difficult to burn completely, and which is very likely to escape from the combustion tube unoxidized. To secure its complete combustion, a *long* and *hot* layer of copper oxide is necessary.

The process requires close attention to details and skill in fitting up and manipulating apparatus. The precautions mentioned under the combustion method for carbon apply equally here, especially as to the purity of the oxygen and the copper oxide. The latter should be examined for $CaCO_3$ or other carbonates which are liable to give up CO_2 on heating, and also for bases which may absorb CO_2. $CaCO_3$ will be decomposed at one temperature, and the CaO formed will absorb CO_2 at another. CuO can be examined for CaO by extracting it with a little dilute HNO_3, adding NH_4OH in excess and then testing the liquid with $(NH)_4C_2O_4$. The "wire" oxide is the best and should be used.

The asbestos used in the tube must be freed from carbonates by treatment with HCl and ignition.

The oxygen must be tested as to its purity, and must not be kept in rubber bags or passed through long rubber tubes.

The Arrangement of the Apparatus.—This is in many respects similar to that used in the determination of the carbon in iron, except that, as the water is to be weighed as well as the CO_2, tubes for absorbing it are added.

The train comprises: First, a gas holder for the oxygen. About 500 c.c. of oxygen are required for each combustion.

Where only an occasional combustion is made, a simple gas holder can be made of a couple of glass bottles.

Second, the purifying train for the air and oxygen. This is made in duplicate. The bottle containing sulfuric acid absorbs the traces of ammonia or its salts, usually present in the air of a laboratory. If these were not taken out they would burn in the tube and form water and make the results on hydrogen too high. As it is as important to purify the air from moisture as from CO_2, in this process, the train is made large and separate U-tubes are used for the soda lime and the $CaCl_2$.

Figure 16 shows the details: *A* is a bottle with moderately concentrated H_2SO_4; *B* is a bottle with about 50 c.c. of KOH solution of 1.27 sp. gr.; *C* is the U-tube with the soda lime and *D* is the U-tube with the $CaCl_2$.

Third, the combustion tube: This should rest on asbestos in the trough of a long gas combustion furnace. The tube should be made of the best infusible glass (preferably Jena) and have an internal diameter of about ½ in. The walls of the tube must not be too thick or they will crack. The ends of the tube should be rounded by heating and should be fitted with good soft corks, well rolled. Rubber connections with this tube are not to be recommended, as they become warm and are liable to give off hydrocarbon vapor and to absorb some CO_2. A long tube and furnace are necessary. The writer uses a furnace with 25 burners and a tube 40 in. long.

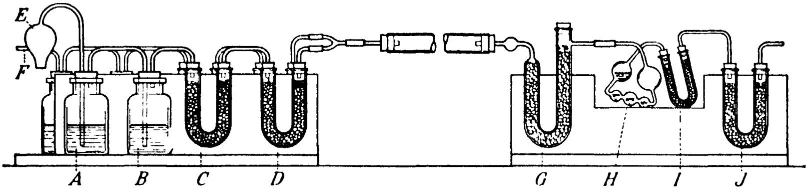

FIG. 16.

The tube is filled as follows: A space of 5 to 5½ in. is left empty at the end nearest the absorbing train. Then follows: (1) a plug of asbestos; (2) 5 in. of fused $PbCrO_4$ in small lumps; (3) an asbestos plug; (4) 12 to 14 in. of pure, recently ignited "wire" CuO (or a close coil of fine copper gauze thoroughly oxidized by heating it in a stream of pure oxygen); (5) an asbestos plug; (6) the "boat" for holding the coal. There must be 13 or 14 in. of empty tube following the last asbestos plug, so that the part of the tube in which the "boat" is placed will be well in the furnace, and yet the tube itself project at least 4 in. outside of the furnace. The end of the tube is connected by a cork, glass tube and rubber connection with the purifying train. The cork connections in the ends of the combustion tube must not become hot enough to run any risk of being burned; hence, a sufficient length of tube must project from the furnace at each end. These projecting ends should be further protected from the heat of the furnace by discs of sheet asbestos 6 to 7 in. in diameter, with holes in the center through which the combustion tube passes.

With a tube arranged as above, it is not necessary to insert a copper coil behind the "boat," as is sometimes directed, provided the coal is slowly heated so as to expel the volatile matter gradually, and that a continuous current of air or oxygen is kept passing through the tube so as to prevent the products of the decomposition from working back, condensing in the cool part of the tube and so escaping combustion.

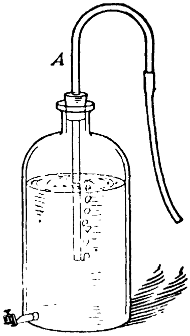

Fig. 17.

Fourth, is the absorbing train following the combustion tube, shown in Fig. 16, and consisting of *G*, a $CaCl_2$ tube, the end of which is inserted into the cork of the combustion tube; *H*, Liebig potash bulbs; *I*, a soda lime-calcium chloride tube similar to that used in connection with the potash bulbs in the determination of carbon in iron; *J*, a guard tube similar to *I* but reversed, which is connected with an aspirator for drawing air through the apparatus. An absorption bottle filled with soda-asbestos, "Askarite," is better than the potash bulbs, *H*.

A "Mariotte bottle," arranged, as shown in Fig. 17 makes the best aspirator. The suction tube *A*, passes in through a rubber stopper at the top and reaches nearly to the level of the run-out tube. By slipping the suction tube up or down, the suction head can be regulated so as barely to overcome the resistance of the train, and will then remain exactly the same as long as the water in the bottle is above the end of the tube, and thus the rate of aspiration can be more easily kept constant.

Testing the Apparatus.—First, see that it is perfectly tight by starting the aspirator and shutting off the entrance of air. Second, heat the tube red hot throughout and aspirate 2 liters. Detach and weigh the potash bulbs and U-tube. Connect up again and aspirate ½ liter of oxygen and then 2 liters of air.

Detach the tubes and weigh. There should be neither gain nor loss of weight. When consecutive weighings are found to agree within 0.5 mg., the apparatus is ready for the analysis.

Process of Analysis.—Ignite and cool the boat. Weigh into it 0.2 gram of the finely pulverized and well-mixed coal. (The sample must be made *very fine*, lest by weighing so small a quantity average results will not be obtained.) Insert the boat into its proper place and connect up the apparatus. Then carefully heat the $PbCrO_4$ to *dull* redness and the CuO to bright redness, drawing a slow current of air through the apparatus all the time. Now heat the tube behind the coal and then the coal itself, cautiously, until the volatile products are slowly driven off and carried forward over the hot CuO. Then introduce oxygen, regulating the supply so as to avoid too vigorous combustion and consequent fusion of the ash, which will lead to retention of carbon. After the carbon is all burned, which is shown by the sudden disappearance of the glow, continue the oxygen for two minutes, then cut it off and aspirate air. Turn off the gas burners and let the tube cool. Continue the aspiration until 1,200 c.c. or more (at least seven times the capacity of the tube and absorbing train) have been drawn through. Now detach the absorption train and weigh. The increase in the weight of the $CaCl_2$ tube gives the water produced. This divided by 9 gives the weight of the hydrogen in the coal. The increase in the CO_2 apparatus is the CO_2; three-elevenths of this is carbon. The apparatus is now ready for another determination, as the CuO will all have been reoxidized by the air current.

The aspiration should be so regulated that not more than two or three bubbles pass through the potash bulbs per second. During the combustion in the oxygen the gas will consist largely of CO_2 and will be almost wholly absorbed, though the flow of oxygen into the apparatus may be quite rapid at the time. Care must be taken that the oxygen supply is sufficient to prevent back suction at this time.

As soon as the CO_2 is absorbed, the gas may begin to run through the potash bulbs too rapidly, unless the gas supply is promptly reduced.

The pressure of the gas in the tube should be kept near that of the atmosphere. This can be accomplished by careful regulation of the gas and the aspirator.

As was noted in the determination of carbon in steel, it is desirable to reduce the necessary aspiration to as small a volume as possible by using small connection tubes and a compact train. This saves time and increases accuracy.

After the boat containing the ash is withdrawn from the tube, weigh it. The ash so determined should agree with that found in the proximate analysis.

The tube should be kept carefully closed with good corks when not in use. A train and tube such as that described can be used for months. A good tube of Jena glass, while it may twist out of shape badly, will not crack or blow if carefully handled. Fifty or more determinations can usually be made on one filling of the tube. The filling of "Askarite" as shown for carbon in steels will last for 20 determinations of carbon in coal.

The Determination of Nitrogen in Coal..—All coals contain some nitrogen, running usually between 1.0 and 1.4 per cent. The nitrogen is present as some compound or compounds derived from the proteid matter of the original vegetation.

When organic matter containing nitrogen is digested in strong sulfuric acid in the presence of mercury, the nitrogen is converted to ammonia as ammonium sulfate and all of the organic material of the coal is completely oxidized. The ammonia can then be distilled out of the sulfuric acid solution by making it alkaline, the liberated ammonia being caught in an excess of standard acid solution and the excess determined by titration.

Procedure.—Transfer 1 gram of the finely pulverized coal to a Kjeldahl flask, add 30 c.c. of H_2SO_4 (sp. gr. 1.84), 7 grams of K_2SO_4 and 0.6 gram of metallic mercury. Heat to boiling and digest until all the particles are thoroughly oxidized and the liquid is nearly colorless. The boiling should be continued at least two hours after the liquid has reached the straw-colored stage. Cool somewhat and add crystals of potassium permanganate, a few at a time, until a permanent green results.

Cool, dilute to 200 c.c. with cold water and transfer to a 750-c.c. distilling flask. To precipitate the mercury, add 25 c.c. of a 4 per cent K_2S solution. Add 1 gram of granular zinc to prevent bumping and enough strong NaOH solution to make the solution distinctly alkaline (the solution should be cold before the NaOH is added and the NaOH solution should be poured down the sides of the flask so as not to mix with the solution.)

Quickly connect the distilling flask to the condensing apparatus. The end of the tube at the exit end of the condenser should dip into the standard acid in a 150-c.c. flask and the tube should contain an enlargement to prevent the standard acid from being sucked into the distillation flask. The tube connecting the stopper of the distillation flask with the condenser should have a trap arrangement to prevent liquid spray from the flask being carried over into the condenser.

Shake the distillation flask to mix the contents and heat to boiling, the boiling being continued until 150 to 200 c.c. of distillate has passed over. The distillate is caught in a flask containing 10 c.c. of standard H_2SO_4 solution, the end of the tube always dipping beneath the surface of the acid. If trouble is experienced from frothing during the distillation, it may be prevented by the addition of a small piece of paraffin.

Remove the receiving flask and titrate the excess of standard acid with a standard NaOH solution, using methyl orange or cochineal as indicator. The acid solution may be conveniently made up so that 1 c.c. equals 0.005 grams of nitrogen or, if a standard decinormal solution is already at hand, it may be used, but in this case 30 c.c. should be used. One cubic centimeter of decinormal acid will neutralize 0.0014 gram of nitrogen as ammonia. The acid may be standardized as directed on page 61.

Notes.—It is absolutely essential that a blank determination be made by going through exactly the same procedure as above, except that 1 gram of pure cane sugar is used instead of coal.

Coke and anthracite must be ground very finely, as they are very difficult to oxidize. Even with fine grinding the digestion may require 12 hours.

The laboratory in which this determination is made must be free from ammonia fumes.

For further details, see *Bulletin* 107 (revised) U. S. Department of Agriculture, Bureau of Chemistry.

THE OXYGEN IN COAL

As no good method is known for the direct determination of the oxygen in coal, it is always determined by difference, the sum of the percentages of H, C, N, S and ash being subtracted from 100 and the remainder called oxygen. The result so obtained is always inaccurate, the error increasing with the percentages of the ash and sulfur. The weight of the ash does not represent that of the mineral matter in the coal, the pyrite in the coal being burned to Fe_2O_3 and the sulfur passing off as SO_2. Thus, 4 atoms of S in 2 FeS_2 is replaced by 3 atoms of O in Fe_2O_3, and the loss of weight is equal to five-eighths of the S. For this reason many chemists use $\frac{5}{8}$ S instead of S in the determination of O by difference. As coals contain sulfur in other forms than FeS_2, and also, frequently, other compounds that lose weight on burning, such as $FeCO_3$ and $CaCO_3$, it is doubtful whether the results obtained in this way are any better than those given by the simple formula first given.

The American Society for the Testing of Materials, in the standards for 1921, gives the formula:

Corrected oxygen $= 100 - [(C - C') + (H - H') + H_2O + S' +$ corrected ash $+ N]$
$C =$ total carbon.
$C^1 =$ carbonate carbon.
$H =$ total hydrogen less hydrogen of water.
$N =$ nitrogen.
$H^1 =$ hydrogen from water in clay, shale etc.
$H_2O =$ water as found at 105° C.
$S' =$ sulfur not present as pyrite or sulfate (usually may be disregarded).
Corrected ash = mineral constituents originally present in the coal.

For most purposes this can be approximated by adding to the ash as found five-eighths of the pyritic sulfur, the CO_2 of carbonates and water of clay, shale.

Tincture of Cochineal.—Coarsely pulverize 2 or 3 grams of cochineal in a small porcelain mortar, moisten with dilute alcohol (1 vol. alcohol to 3 vols. water) and transfer to a funnel containing a 9 cm. filter paper. When the alcohol has run through wash with successive small portions of 25 per cent. alcohol until about 20-25 c.c. have run through and most of the color is extracted. Now dilute the colored extract with 25 per cent. alcohol to about 100 c.c. for each gram of cochineal taken. This mode of extracting with a small quantity of alcohol avoids the solution of much of the material other than the color. The solution keeps much better than when the whole of the alcohol is used in extracting as is sometimes directed.

CHAPTER XXXVII

DETERMINATION OF THE FUSIBILITY OF ASH

This determination is of as great importance as the determination of the amount of ash. The usability of a coal or coke in gas producers, water gas generators, steam boilers and even in domestic furnaces is profoundly affected by the way in which the ash resists high temperature. A clinkering ash is very harmful to the action of gas producers and water gas generators and is costly in the operation of a steam boiler plant.

Coal ash is composed largely of quartz, kaolin, oxides of iron, lime and magnesia, usually within the following limits:

Constituents	Per Cent	Constituents	Per Cent
SiO_2	40 to 60	CaO	1.0 to 15
Al_2O_3	20 to 35	MgO	0.5 to 4
Fe_2O_3	5 to 25	$Na_2O + K_2O$	1.0 to 4

The fusibility of coal ash depends on several factors, such as the ratio of the silica to the bases present, the particular bases and the percentage of alumina present. Mixtures extremely high in silica or extremely high in bases are not readily fusible. Ash that is low in iron is usually so highly siliceous that it is not readily fusible. Ash from coals high in pyrite is necessarily high in iron, and the ratio between the bases and silica is often such that easily fusible compounds may be formed. As a rule, coals containing considerable sulfur in the form of pyrite are apt to give trouble from clinker formation. Under conditions of the fuel bed, the iron of the pyrite is apt to be converted to ferrous oxide, which, with the silica present, forms ferrous silicates which fuse at comparatively low temperatures.

The No. 3 melter's furnace of the American Gas Furnace Company is excellent (Fig. 18). This furnace is a type of pot furnace especially suitable for fusion determination, as the three burners arranged on a tangent near the base of the furnace produce a rotary flame which completely surrounds the crucible in which the cones are placed. The whirling flame heats the crucible uniformly, and when an excess of gas is used, a reducing atmosphere is maintained within the crucible, giving the lowest point at which the ash fuses. The air is supplied at an approximate pressure of 3 lb. per square inch, and the gas used may be either natural or artificial.

The furnace proper consists of three easily replaceable parts of fire clay, namely, a lower cylinder containing the three tangential tuyeres and forming the bottom of the furnace; a removable upper cylinder 7 in. in internal diameter and 7 in. high; and a cover plate 1½ in. thick having a vent hole in the center for the flue gas.

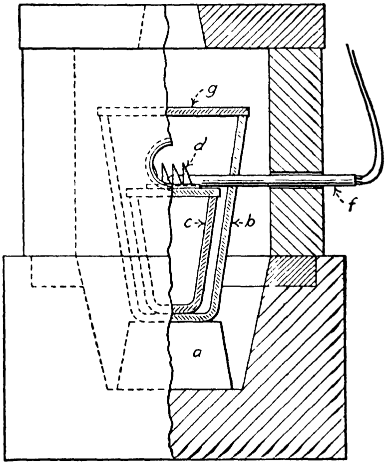

Fig. 18.

The stock design is modified by providing the upper cylinder with two holes in the side; one is a 2-in. observation hole with its center 4 in. from the top of the cylinder (excluding the cover plate) and the other is a 1-in. thermocouple hole 90° to the right of the observation hole. The bottoms of these two holes are in the same horizontal plane. The interior of the furnace is cylindrical and approximately 7 in. in diameter and 11 in. high. A counterbalanced sheet-iron canopy is connected with a telescopic 8-in. flue to an exhaust system for conducting the hot gases out of the room.

We have found that a homemade furnace similar to the above works very satisfactorily.

In this department, when testing fusibility of ashes which are extremely refractory, we use a molybdenum-wound electrically heated furnace through which is passed a gas stream composed of 50 per cent hydrogen and 50 per cent H_2O vapor. (See FIELDNER A. C., "Fusibility of Ash from Coals of the United States," U. S. Bureau of Mines, *Bull.* 209.)

Furnace.—The interior of the furnace as arranged for making a test is shown in Fig. 18. The ash cones *a* are supported on a plate of alundum cement serving as a cover for the crucible *b*, which is a Denver fire-clay, hard-burned crucible, No. E, 4 in. high and 3 in. in diameter at the top. An alundum tube of the proper height may be used in place of crucible *b*. Crucible *d* is a Denver fire-clay, hard-burned crucible, No. K, 7¼ in. high and 4⅝ in. in diameter at the top; it has observation and thermocouple holes corresponding to those in the furnace cylinder, and it rests on a fire-clay support. The thermo element is protected by a glazed Marquadt porcelain tube *e*, ¼ in. in diameter. A fused silica tube, 1⅞ in. in external diameter and 6 in. long, is placed in the observation hole of the furnace, the inner end being flush with the inside furnace wall and the other end projecting from the furnace. This crucible should be provided with two holes in the side, an observation hole 2 in. in diameter with its center 2 in. from the top of the crucible and a thermocouple hole 1 in. in diameter, 90 deg. to the right of the observation hole. The bottom of this hole should be in the same horizontal plane as the bottom of the observation hole. The hard-burned, fire-clay crucibles will not withstand a temperature exceeding 1,500° C. The average life of a fire-clay crucible under these conditions is about six runs.

Corundite crucibles and covers made by the Massillon Stone and Fire Brick Company are longer lived than the fire-clay crucibles, being good for about fifty runs to temperatures not exceeding 1,500° C.

Preparation of Coal Ash.—Spread out 50 to 100 grams of 60-mesh coal on a 5-in. fire-clay roasting dish, and completely convert it to ash in a muffle furnace at a temperature of 800 to 900° C. Transfer 5 to 10 grams of this ash to an agate mortar and grind to a fineness of 200-mesh. A mechanical agate-mortar grinder will save time where many determinations are made. Place the finely ground ash in a silica or porcelain capsule, about ⅝ in. deep and 1¾ in. in diameter, and ignite for two hours in a current of oxygen, at a temperature of 800 to 850° C. The purpose of this ignition is to insure complete and uniform oxidation of the ash.

Preparation of the Cones.—Moisten the ignited ash with a 10 per cent dextrin solution, containing a small amount of salicylic acid as a preservative, and work into a plastic mass with a spatula. Mold the plastic material into small triangular pyramids ¾ in. high and ¼ in. wide at each side of the base. The pyramids are made by firmly pressing the plastic material with a steel spatula into a brass mold of the dimensions mentioned. Strike off the surface smooth and remove the cone from the mold by applying a small knife blade at the base. Mount the cones when dry in a refractory base composed of a mixture of equal parts of kaolin and calcined alumina. Moisten the base mixture to make it workable, and spread a part of it out on a sheet-iron plate. Then mount the cone in a vertical position in a small hole made in the base, and put a little of the base material into the hole around the bottom of the cone to fill the crevices and to make the cone stand firmly. Usually several cones are mounted on one base. Dry the sheet-iron plate with the test piece on a hot plate, then ignite the cones at a dull-red heat for 30 minutes in an open muffle to remove carbonaceous material.

Method of Heating.—Put the test piece in the muffle furnace in the position shown in Fig. 18, place the loosely fitting cover *c* on the crucible and ignite the gas. It is necessary to let the gas burn about 10 minutes to heat the furnace parts before the large cover plate of the furnace is replaced; otherwise the flame is apt to blow out. After the cover plate of the furnace has been put in position, the flow of gas and air is increased enough to cause combustion to take place just above the tuyeres and yet maintain a yellowish flame at least 6 in. above the opening in the furnace cover plate. While such a flame is maintained above the furnace, gradually increase the temperature by a suitable adjustment of gas and air to 800° C., then reduce the rate of heat increase to not less than 5 and not more than 10° C. per minute. Maintain this rate until the end of the test. It is also important that the 6-in. reducing flame be maintained at the furnace vent throughout the test, if possible, and at all events up to a temperature of 1,450° C. Temperatures above 1,450° C. require larger proportions of air to gas; however, a strongly reducing atmosphere is not so essential at the higher temperatures, as refractory ashes, owing to their low iron oxide content, are only slightly affected by oxidizing or reducing atmospheres. After a test has been completed, turn the supply of gas and air off gradually, to avoid cracking the muffle crucible.

The softening temperature is defined as the temperature at which the cone has fused down to a spherical lump.

The permissible differences of the softening temperature point in duplicate determinations are as follows:

Same analyst	30° C.
Different analysts	50° C.

Notes.—Critical points other than the softening temperature, which may be observed during the test, and which may be of value are as follows:

The Initial Deformation Temperature.—The temperature at which the first rounding or bending of the apex of the cone takes place. This laboratory always reports the temperature of incipient fusion and the temperature of complete fusion.

It is necessary to maintain a reducing atmosphere as above directed with an excess of gas, because the fusion temperature is profoundly affected by the condition of oxidation of iron. Ferric oxide and ferric silicate are infusible at the temperature of this furnace. On the other hand, ferrous oxide is an excellent flux and its presence greatly lowers the fusion temperature of coal ash.

For a thorough discussion of the principles of physical chemistry underlying the fusion temperatures and equilibria of oxides and silicates, a careful study of the following should be made.

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CHAPTER XXXVIII

THE DETERMINATION OF THE HEATING POWER OF COAL

The discussions and directions in this chapter are largely taken from Prof. E. E. Somermeier's work as recorded in his book "Coal." Prof. Somermeier's lifetime of work on the testing of coal in this Department of Metallurgy at the Ohio State University has justified this literal quotation from his book.

By the heating power of a fuel is meant the total amount of heat produced by the complete combustion of the unit weight of the fuel.

In order to simplify calculations in technical work, it is convenient to define the unit of heat as the heat required to raise the unit weight of water the unit of temperature. If the unit of weight is the gram and the unit of temperature the degree Centigrade, the unit of heat is the calorie. If the units are the pound and the degree Fahrenheit, the heat unit is the British thermal unit.

With the heat unit defined as above, the number expressing the heating value of a fuel will be the same, whatever the unit of weight adopted, as long as the unit of temperature is unchanged. If the unit of temperature is changed, as, for instance, from Centigrade to Fahrenheit, the figure for the heating value will simply have to be changed in the inverse ratio of the dimensions of the units.

In the example quoted, as the ratio of the degree Centigrade to the degree Fahrenheit is $\frac{100}{180}$, heating powers in calories can be converted into heating powers in B.t.u. by multiplying them by $\frac{180}{100}$ or $9/5$.

The establishment and use of specifications for the purchase and sale of coal, based upon the heating value, require the actual determination of the heating value of the sample or samples which are used as the basis of settlement, and in analyzing such samples the chemist is expected and required to make this determination along with the determination of moisture, ash and sulfur. At present some form of pressure calorimeter, in which the sample is burned in a steel bomb under 15 to 25 atmospheres pressure of oxygen, is generally regarded as the standard type of calorimeter, and specifications for the purchase of coal frequently specify that the heating value shall be determined in a bomb calorimeter. Some of the commoner types of this form of calorimeter are: the Mahler, the Atwater, the Emerson, the Williams and the Parr.

The details of the method of making a determination and the calculation of the results are as follows: This description is based primarily upon the use of a Mahler calorimeter but is applicable with minor modifications to any of the other calorimeters mentioned. About 2 grams of the 60-mesh sample are pressed into a small briquet by means of a small screw press and mold. The press used by the writer is the iron frame of a 2-quart tincture press manufactured by the Enterprise Manufacturing Company of Philadelphia, Pa. After removal from the mold, the briquet is broken into smaller portions and about 1 gram accurately weighed and placed in the platinum or nichrome combustion tray which is covered with a thin disc of asbestos paper which has been washed with hydrochloric acid and ignited in a muffle furnace. The tray is then attached to one of the platinum terminals fitted to the lid and the terminals are connected by a piece of iron or nichrome wire (platinum wire should be used when the bomb is platinum lined) about 10 cm. long and formed into a spiral. The ends of the wire are attached to the clean platinum terminals, by wrapping the wire tightly around them. The spiral is bent down so that it touches the coal sample in the tray. The lid is placed on the bomb and screwed down tightly against the lead gasket. Oxygen under pressure is admitted gradually into the bomb through the valve stem until the manometer recording the pressure reads 18 to 20 atmospheres. The needle valve is then closed. Very little force should be used in closing it and extra pressure should be avoided.

The bomb *B* (Fig. 19) filled with oxygen is placed in the brass bucket containing from 2,400 to 2,500 grams of distilled water, the bucket having been previously placed in the insulated jacket. The stirring apparatus *S* is then adjusted so that it touches neither the bucket nor bomb and works freely. The thermometer *T* for recording the temperature rise is clamped into position and so adjusted that the lower end of the mercury bulb is about 5 cm. above the bottom of the bucket. The outside terminals of the bomb are connected with wires leading to the switch. The stirrer is then set in motion and the readings of the thermometer taken by means of a telescope attached to a cathetometer. The thermometer is graduated to $\frac{1}{50}$th° C. and the readings can be interpolated to thousandths of a degree. The stirring should be continued at a uniform rate throughout the determination and should be sufficiently rapid to insure thorough mixing. Preliminary readings are taken at intervals of one minute each for about five minutes, or until the rate of change per minute is nearly uniform and a definite rate is established. The switch is then closed and the current turned on for about one-half second. The ignition of the sample is followed by a very rapid increase in temperature and the first two readings after combustion are taken one-half minute a part. Other readings are then taken at minute intervals. The temperature usually reaches a maximum in three or four minutes, but the series of readings is continued until a uniform final rate has been established. Not less than five and sometimes as many as seven or eight readings are required to determine the final rate.

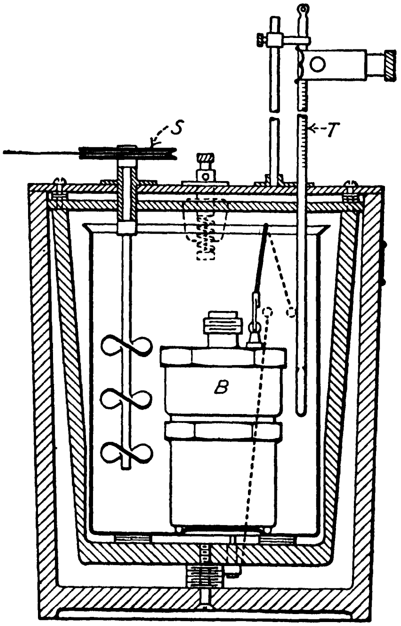

Fig. 19.

The calculations involved and corrections applied are shown by a typical determination on p. 285.

The readings from 7–50 to 7–54 are the readings of the preliminary period. The increase in temperature during this time is 19.318 to 19.348 = 0.030, or 0.0075° per minute. The switch was closed and the combustion started at 7–54, the maximum observed temperature being at 7–57. From 7–58 to 7–64 the rate of loss is quite regular. Inspection shows this loss to be about 0.004° per minute. The temperature at 7–58 is taken as the end of the combustion period, since it is the first reading

FORM FOR CALORIMETER DETERMINATIONS

Department of Metallurgy, Ohio State University

SAMPLE No. 5160 Date—5-24-1912

Wet and dry bulbs = 14-22°C. Coal = 1.0018 grams
Jacket water = 21° C.
Room temperature = 22° C.

Time.	Readings ° C.		Observed final temperature...	21.744
			Observed initial temperature.	19.348
7-50	19.318			
51	19.326		Observed temperature rise...	2.396
52	19.334	= +0.0075	Radiation correction........	= +0.0094
53	19.340		Calibration correction.......	= −0.006
54	19.348	+0.0075	Stem correction.............	= +0.0014
		+0.0026		
½	20.2	+0.0030	Corrected temperature dif...	= 2.4008
		+0.0001	Water equivalent 1°........	=2,875
55	21.40	−0.0028		
		−0.0035		5,750.0
56	21.700	−0.0043		1,150.0
		−0.0043		00.0
57	21.746	−00.043		00.0
		−0.0043		2.3
		−0.0043		
58	21.744		Calories of heat developed..	=6,902.3
59	21.740	−0.0094	Corrections...............	= 101.6
60	21.736			
1	21.734	= −0.0043	Heat from sample..........	=6,800.7
2	21.728		Correction for excess sample	
3	21.722		over 1 gram.............	= 12.2
4	21.718			
			Calorific value of coal......	=6,788.5

Wire fuse = 10 cm.
Wire fuse unburned = 2 cm.
Wire fuse burned = 8 cm. (cm. = 2.4 cal.) = 19.2 cal.
Titer, 23.8 to 31.6 = 7.8 c.c. (1 c.c. = 5 cal.) = 39.0 cal.
Sulfur in coal 3.34 per cent (.01 g. = 13 cal.) = 43.4 cal.

Total correction = 101.6 cal.

Thermometer used, No. 5764 Position 5 cm.
Scale reading 18.3. Stem temperature 22° C.
Atmospheres oxygen used = 18 Valve—tight.
At 19° add 4.5 c.c. of water to obtain 2,400 grams.

(Signed) F.M.D.———

Checked M.D.———

that falls in line with this rate of loss. The loss during the six minutes following the combustion period is 21.744−21.718=0.026, or 0.0043° per minute. The observed temperature increase is the difference between the temperature at the beginning and end of the combustion period, or 21.744−19.348=2.396°. The total change in the rate of gain or loss in the system corresponding to 2.39° increase of temperature is from a rate of +0.0075 to a rate of −0.0043, a total change of 0.0118°. A change of rate of 0.0118 with a change of temperature of 2.4° (counting to the nearest 0.1°) is equivalent to a change of rate of approximately 0.0005° for each 0.1° temperature change, from which the rate of gain or loss at the different readings can be obtained. The rate of gain or loss at the 58th minute is the final rate −0.0043. The temperatures at the 57th and 56th minutes are within 0.1° of the temperature at the 58th minute and the rate of loss is the same as that at the 58th minute. The temperature at the 55th minute is approximately 0.3° lower and the rate of loss is, accordingly, less by $0.3 \times 0.0005° = 0.0015$, or the rate of change at the 55th minute is $-0.0043+0.0015=-0.0028°$. At 54½ minutes the temperature to the nearest 0.1° is 0.9° higher than at the 54th minute. The rate of change corresponding to 0.9° is $9 \times 0.0005 = 0.0045$. Subtracting this change from the rate of change at the 54th minute = +0.0030. The actual temperature gain or loss for each of the different intervals is found by adding the rates at the beginning and end of the interval and dividing by 2, if a minute interval, or by 4, if a half-minute interval. The sum of the rates at the beginning and end of the interval from 54 to 54½ is $+0.0075+0.0030=+0.0105$. This divided by 4 and carrying the result to the nearest fourth decimal = +0.0026°, the temperature gain during the interval. For the interval 54½ to 55, $+0.0030+(-0.0028)=0.0002$. This divided by 4 gives 0.00005, or to the nearest fourth decimal = +0.0001°. For the minute interval 55 to 56, $-0.0028+(-0.0043)=-0.0071$. This divided by 2 = −0.0035°. The losses in the other intervals are obtained in a like manner. Adding together the different gains and losses, the total loss is found to be 0.0094, from which the radiation correction = + 0.0094°. The calibration correction for the thermometer used = −0.0060°. The stem correction = +0.0014°. The corrected temperature difference $=2.4008°$. The water equivalent of the calorimeter system is 2,875 cal. Multiplying the corrected temperature change by this water equivalent (*i.e.*, by the number of calories necessary to cause a rise of 1° of temperature), the total heat developed during combustion is $2.4008 \times 2{,}875 = 6{,}902.3$.

Corrections.—The heat from the burning of the wire fuse is found by multiplying the weight of wire taken by its calorific value (1,600 cal. per gram $=2.4$ cal. for 1 cm.) $8.0 \text{ cm.} \times 2.4 = 19.2$ cal. When nichrome is used, no correction for wire is necessary. The acidity of the bomb liquor after combustion is found by titrating it with a standard ammonia of such strength (0.0059 grams of ammonia per cubic centimeter, see acidity corrections) that 1 c.c. corresponds to a heat correction of 5 cal., assuming the acidity to be entirely due to nitric acid, from which 7.8 times 5 equals 39 cal., the correction due to the formation of nitric acid.

A large part of the acidity in high-sulfur coal is, however, due to sulfuric acid, and the heat correction for acid formed, considering it all as nitric acid, is, therefore, incomplete, a further correction of 13 cal. for each 0.01 gram of sulfur present being required. (See acidity corrections.) In the sample 3.34 per cent sulfur is 0.0334 gram sulfur on a 1-gram sample taken. Therefore, the correction is $3.34 \times 13 = 43.4$ cal.

The total of these corrections is 101.6 cal. The total heat developed, 6,902.3, less this correction of 101.6 gives 6,800.7 cal. of heat from the combustion of the coal. These 6,800.7 cal. are developed by 1.0018 grams of sample. The value per gram is, therefore, 6,800.7 divided by 1.0018. The amount of sample taken is so near 1 gram that this correction can be approximated as 0.68 of a calorie for 0.0001 gram of coal. For 0.0018 the correction is, accordingly, $18 \times 0.68 = 12.2$. Making this correction gives 6,788.5 as the calorific value of the coal.

The foregoing description of the calculations makes them appear more difficult and troublesome than they really are, as practically all the corrections can be made mentally, and the radiation corrections can be determined very readily if the calculator is familar with the routine of the determination. The use of printed blank forms saves time and insures regularity and completeness in the records.

SPECIAL NOTES ON CALORIFIC DETERMINATION

Complete Combustion of the Sample.—To insure complete combustion, from three to five times the theoretical amount of oxygen required should be used, which, for a 1-gram sample of coal, is equivalent to approximately from 9 to 15 grams of oxygen. In a bomb of the Mahler type, with a capacity of 600 c.c., the author has found it unsafe to use less than 15 atmospheres pressure of oxygen, which corresponds to about 11 grams of oxygen, and, in ordinary work, 18 to 20 atmospheres, corresponding to about 15 grams of oxygen, are preferable. The complete ignition of the briquetted sample is more certain if the briquet is not made too hard and is broken up into a number of pieces. The fine sample can be weighed direct and the combustion made upon the coal in this condition if care is used, in admitting the oxygen to the calorimeter, not to blow any of the fine coal out of the tray. On account of this danger of blowing out fine coal, the author prefers briquetting most samples. Anthracite coal and coke will not briquet readily and require to be run in powdered form. The use of a disc of ignited asbestos on the tray to lessen the rate of conduction of heat during combustion is a decided advantage in securing complete combustion of cokes and anthracites which are much more difficult to burn than the ordinary bituminous coals.

Preventing Leakage of Valve.—By use, the valve through which the oxygen is admitted into the calorimeter soon becomes corroded from the action of the acid fumes and rusted through the action of moisture and air. In this condition it is extremely difficult to prevent considerable leakage of oxygen. This leakage may be prevented and the valve made to fit tight by cutting a thin washer of lead about $\frac{1}{32}$ in. in thickness and fitting into the valve, using care in its insertion not to get it in crosswise and thereby close the opening into the bomb. A very efficient way to insert it is as follows: Hold the valve stem, valve end up and slip the washer over the tip of the needle. Then with the stem in this vertical position screw the lid onto the stem carefully till the washer is pressed into place. Very slight pressure is required to close the valve when fitted in this way and extra pressure is to be avoided as tending to force lead into the needle opening, which may be entirely closed and will, in this event, require drilling out before the bomb can be used again. These valve troubles are not experienced with the Parr bomb.

Leakage around the Lid.—As a rule, little trouble is experienced from leakage around the lid if the lead gasket is kept smooth. Moistening the gasket with a drop of water before putting on the lid considerably lessens the danger of leakage. The film of water between the gasket and the lid of the bomb appears to be of considerable advantage in securing a gas-tight joint.

Water Surrounding the Bomb.—In the regular routine determinations the amount of water used is more conveniently measured than weighed. For this purpose the author uses a Florence flask holding about 2,400 c.c. of water when filled to the middle of the neck. The number of grams of water which it delivers is determined by filling it to a fixed mark and weighing at a definite observed temperature. The flask is then emptied and allowed to drain 15 seconds and again reweighed, an allowance of 2.4 grams being made for the effect of the buoyancy of the air displaced by this amount of water. The difference in weight is the number of grams of water the flask delivers at this temperature. A table is then prepared giving for different temperatures the number of cubic centimeters of water which must be added to the water inside of the flask to obtain 2,400 grams.

The diameters of the necks of the flasks used are from 1¼ to 1⅜ in. With this size of neck and a uniform time of 15 seconds for drainage, the amount of water can easily be measured to an accuracy of 1 c.c. and the maximum errors of measurement do not effect the calorific value obtained over 2 or 3 cal. The time required for measuring is less than that required for weighing and does not involve the continued use of an expensive balance and set of weights.

An example of the method of calibration is as follows:

	Grams
Weight of flask filled with water to a definite mark	=2,842 5
Weight of empty flask after draining 15 seconds	= 450.5
Difference	=2,392.0
Corrections to weights	= + .6
Corrections for buoyancy of air	= +2.4
Total weight of water delivered	=2,395.0

Temperature of water = 20° C. For small corrections, 1 c.c. of water may be taken as equal to 1 gram, and at the temperature of 20° C. the amount of water to be added to the flask in order that it may deliver 2,400 grams is 5 c.c. The amounts for other temperatures based on the specific gravity of water at the different temperatures are obtained as follows:

The volume of the flask in cubic centimeters = 2,395, divided by the specific gravity of water at 20° C. is $\frac{2,395}{0.99823} = 2,399.2$.

The densities of water for the range covered by ordinary calorimetric work are as follows:

Degrees C.		Density	Degrees C.		Density
8°	=	0.99988	20°	=	0 99823
10°	=	0.99973	22°	=	0.99780
12°	=	0.99953	24°	=	0.99732
14°	=	0.99928	26°	=	0.99680
16°	=	0.99898	28°	=	0.99626
18°	=	0.99863	30°	=	0.99567

The weight of the water which the flask will deliver when filled to the mark at any temperature t = the volume of the flask (2,399.2) times the density of the water at temperature t. The amount of water to be added at any given temperature when the flask is filled to the mark is 2,400 minus what the flask holds at that temperature. At 10° this particular flask holds $2,399.2 \times 0.99973 = 2,398.6$. Hence, the correction to be added $= 2,400 - 2,398.6 = 1.4$ grams, or 1.4 c.c. Such a table of corrections once prepared is pasted on the side of the flask and the proper amount to add for any particular determination readily determined.

Temperature Conditions.—More satisfactory rates of gain or loss during a determination are secured if the temperature differences between the air of the laboratory and that of the water inside the inner bucket and in the outer insulating jacket are kept small. The author's practice is to keep the temperature of the water in the outer jacket within a few degrees of room temperature. The water to be used in the inner bucket is cooled till its temperature is about 2 to 3° lower than that of the water in the outer jacket, care being taken that this temperature is not too near the dew point. In warm, damp weather, to avoid this danger, the water in the outer jacket is kept several degrees above room temperature.

With these temperature relations, the greater rate of change during a determination is before the combustion, and the rate of change after the combustion period is small. The larger the rate of change the larger is the possible error. The effects of the larger rate before the combustion period are, after the first minute, practically eliminated. By the end of the first minute most of the total temperature rise has occurred and the rate of change during the other minutes of the combustion period approximates in value the final rate. With the final rate small, the total corrections are correspondingly small and errors from this source are reduced to a minimum.

CORRECTIONS TO BE APPLIED

Correction for Nitric Acid.—The data and calculation of the correction are as follows: In burning the sample in the bomb calorimeter, under pressure, a portion of the nitrogen in the fuel and perhaps some of the nitrogen in the small amount of air in the bomb is burned to N_2O_5 *aqua,* while in combustion of fuel under a boiler the nitrogen either escapes as free nitrogen or burns to gaseous N_2O_5 and passes off in the flue gases. The heat of formation of N_2O_5 *aqua* is approximately 1,020 cal. per gram of nitrogen. The heat of liberation of the nitrogen, as free nitrogen, from the coal is not definitely known, but is presumably not far from 0. The heat of the formation of gaseous N_2O_5 from nitrogen and oxygen is approximately -36 cal. per gram of nitrogen. In either case, the heat change per gram of nitrogen is small and, in correcting for the amount of nitric acid in the bomb, the heat of formation of N_2O_5 *aqua* is usually taken as the nitric acid correction. The reaction for neutralization of nitric acid by an alkali is as follows:

$$2HNO_3 + 2NH_4OH = 2NH_4NO_3 + H_2O,$$

from which it follows that 14 parts by weight of nitrogen as nitric acid equal, in neutralizing value, 17 parts by weight of ammonia (NH_3). A convenient strength for the titrating alkali is 1 c.c. equivalent to 5 cal. of heat. Since 1,020 cal. are produced by the combustion of 1 gram of nitrogen, then 5 cal. are produced by the combustion of $\frac{5}{1,020}$ gram = 0.0049 gram; 0.0049 gram of nitrogen as nitric acid requires $^{17}/_{14} \times 0.0049$ gram of ammonia for neutralization = 0.00595 gram of ammonia per cubic centimeter or 5.95 grams per liter. 1 c.c. of 0.25 N alkali = 3.5 calories.

Correction for Sulfuric Acid.—Any sulfuric acid present is titrated with nitric acid and its heat of formation is partially allowed for by considering it as nitric acid. The data for determining the amount of correction necessary and the amount which is allowed for by considering it as nitric acid are as follows: The heat of formation of aqueous sulfuric acid in the calorimeter is approximately 4,450 cal. per gram of sulfur. In ordinary combustion in air, the sulfur is burned to sulfur dioxide, the heat of formation of which is approximately 2,250 cal. per gram of sulfur.

The excess heat due to the formation of sulfuric acid in the bomb is, therefore, 4,450 − 2,250 = 2,200 cal. per gram of sulfur. In neutralizing with ammonia, the reaction for sulfuric acid is as follows: $H_2SO_4 + 2NH_4OH = (NH_4)_2SO_4 + H_2O$, or, in titrating, $H_2SO_4 = 2HNO_3 = 2NH_4OH$. Expressed by weight, 32 parts of sulfur as sulfuric acid = 28 parts of nitrogen as nitric acid = 34 parts of ammonia (NH_3). Since 32 parts of sulphur as sulfuric acid = 28 parts of nitrogen as nitric acid, 1 gram of sulfur = $^7/_8$ gram of nitrogen in the titration of nitric acid with ammonia. Seven-eights of 1,020 cal. = 892 cal. as the correction which is applied when sulfuric acid is titrated as nitric acid; 2,200 − 892 = 1,308 cal. per gram of sulfur as an additional correction which should be applied. This amounts to approximately 13 cal. for each 0.01 gram of sulfur, or, when a 1-gram sample is burned in the calorimeter, 13 cal. for each per cent of sulfur present in the sample. As the amount of sulfur is frequently as high as 4, 5 or 6 per cent, this correction is often large and there is no valid reason for omitting it, notwithstanding the statement often seen in print that the correction for the sulfur present is never important.

Ignition of the Iron Wire.—In igniting the wire fuse, a current of 3 or 4 amp. is usually required and an e.m.f. of 15 to 20 volts is desirable. Lower voltage, such as a current from 4 or 5 dry cells or from a storage battery, may be used but a low voltage requires special care in making the connection, or failure to ignite often results. If a current of low voltage is used, better contact between the platinum terminals and the wire is secured if the rods and wire are carefully cleaned with emery paper. Moistening the connection between the terminals and the wire with a drop of dilute calcium chloride solution is also an advantage in securing certainty of ignition. The usual laboratory practice of using a high-voltage current, such as the current from a 110-volt lighting circuit, is liable to result in errors by leakage of the current after ignition of the wire, and it is much safer to introduce a resistance coil in parallel with the calorimeter and shunt off only a portion of the current through the igniting wire. In this way the voltage through the calorimeter can easily be cut down to 20 volts.

A convenient resistance for furnishing the proper amount of current from a 110-volt lighting circuit is to mount four 32-cp. lamps in parallel. This will give in the neighborhood of 3½ to 4 amp. of current, which is ample for the size of wire usually used. With this arrangement a 5- or 6-ohm resistance coil of German silver or other high-resistance wire, as nichrome or climax wire, used in parallel with the calorimeter is a simple way of reducing the voltage. Whatever be the connection, the circuit should be kept closed only long enough to insure burning of the wire. This should not require, at most, more than one or two seconds. If more time is required, more current should be used. With leakage of current through the calorimeter, and using the current direct from a 110-volt circuit, as much as 20 cal. per second may be transmitted to the calorimeter, which is an error too large to be neglected. By using the shunt and keeping the voltage below 20, the heat from 4 amp. of current cannot exceed 4 cal. per second, and for the time that the circuit is usually closed it is a small error compared to the possible large one which may be introduced by using the 110-volt circuit direct.

Heat Developed While the Circuit Is Closed for Ignition of the Iron Wire.—The iron ignition wire used (about 0.12 mm. in diameter and about 3 cm. between the terminals), if in good contact with the platinum terminals, has a resistance of less than 1 ohm and the amount of heat developed during the fraction of a second that the current passes through the wire before it ignites is small. The resistance of the calorimeter itself with the insulation in good condition is several millions of ohms. A test on one of the calorimeters indicated a resistance of upwards of 20,000,000 ohms, the test being made on a 120-volt circuit. Pure water is such a poor conductor that, after immersion of the calorimeter in water, the resistance is still high (expressed in thousands of ohms).

In routine work the distilled water used to surround the calorimeter bomb is used over and over again. The resistance of this water, owing to traces of impurities, is not so great as that of the original distilled water, but its resistance is still high. Tests with water which had previously been used in making 40 or 50 calorimeter determinations showed with a 120-volt circuit about 1,500 ohms' resistance. Tests with distilled water taken directly from the laboratory supply showed a resistance of about 5,000 ohms. With the resistance in excess of 1,000 ohms, the heating effect due to leakage of current is quite small and the danger from excessive leakage is either from defective insulation of the bomb itself or from the use of water containing more than traces of impurities. The possible heating effects under these conditions are discussed in the next paragraph.

The heat developed in a conductor of which the resistance is R ohms by a current of I amp. in a time of t seconds is $0.2387RI^2\,t$ cal.

Using the current from a 110-volt circuit with four 32-cp. lamps in parallel, the greatest current is approximately 4 amp. With the resistance coil (5 ohms' resistance) in the circuit, the possible heat developed by passage of current through the calorimeter is small. Before the ignition of the iron wire with a low resistance in the calorimeter circuit (a fraction of an ohm), practically all the current passes through the calorimeter, but since I cannot exceed 4, I^2 cannot exceed 16, and, with the resistance less than 1 ohm, the product of $0.2387RI^2$ is less than 4 cal. per second.

After the ignition of the iron wire under normal conditions the resistance of the calorimeter circuit is expressed in thousands of ohms, and practically all the current passes through the coil having only 5 ohms' resistance. With a resistance of 1,500 ohms, such a small portion of the current flows through the calorimeter that its heating effect is less than $\frac{1}{10}$ cal. per second. With defective insulation in the calorimeter, or with very impure water, the resistance may be very much less and the possible effects under these conditions should be considered.

Water Equivalent of the Calorimeter.—The accuracy of the calorimetric values obtained is to an important degree dependent upon the accuracy with which the water equivalent of the apparatus has been determined. This may be determined by several methods:

1. From the weights of the different parts by multiplying each by its respective specific heat. The water equivalent is equal to the sum of the specific heats of the different parts.
2. By adding definite weights of warmer or colder water to the system and noting the corresponding increase or decrease in temperature.
3. By combustion of the same weight of material but varying the amount of water used.
4. By electric methods.
5. By combustion of a substance of known calorific value, as naphthalene, benzoic acid or cane sugar.

The author's experience with the first three of these methods has not been very satisfactory. The fourth method requires instruments and equipment beyond the reach of most commercial and technical laboratories and practically the only available method which is satisfactory is that of the determination by combustion of a substance of known calorific value. At present the materials available are naphthalene, benzoic acid and cane sugar, samples of which, together with certificates of their heating values, can be obtained from the U. S. Bureau of Standards.

The calorific values of these materials as given by different authorities are as follows:

Naphthalene:	
U. S. Bureau of Standards (standard sample)	9,622
Benzoic acid:	
U. S. Bureau of Standards (standard sample)	6,320
Cane sugar (sucrose):	
Stohmann	3,955
Berthelot	3,961
Fischer and Wrede	3,957

The equation for determination of the water equivalent X of the bomb, bucket, stirrer, etc. is as follows:

(Grams of water + X) × temperature rise = the amount of sample × the calorific value + the heat due to the ignition of the fuse + the heat due to the formation of nitric acid.

Carefully determined water equivalents based upon a number of determinations upon two or more of the standard materials ought to have not only relatively high accuracy but enable different laboratories to work upon a common basis and make their results comparable.

Errors in the Graduation of the Thermometer Used.—These errors, if not corrected for, may be considerable and every calorimeter operator should take some means of insuring the elimination of a greater part of the errors, or at least assuring himself that the errors are not large enough to affect the accuracy of the results materially. The thermometers (whether mercurial or of the electric resistance type) should by all means be sent to the U. S. Bureau of Standards for standardization.

Stem Temperature Corrections.—(Corrections should be made to the observed temperature readings on account of differences between the temperature of the emergent stem and the temperature of the liquid surrounding the bulb.) Most thermometers are graduated and calibrated for total immersion of the stem and bulb. As ordinarily used in calorimetric work, a portion of the stem containing the mercury column always projects above the water and is usually either colder or warmer than the temperature of the water surrounding the bulb. Hence, to secure readings for total immersion, a correction must be applied. As ordinarily expressed, this correction is $N(T-t) \times 0.00016$, where N = degrees of thread above the liquid, t = the temperature of the stem as observed by an auxiliary thermometer, T = the temperature of the bulb and the factor 0.00016 = the difference between the expansion of glass and mercury for 1°C.

From these values the corrections for any conditions usually found can be approximated readily to about 0.001°. To secure this degree of accuracy, N and $T-t$ need be read to only the nearest 0.5° and the observed temperature rise need not be closer than 0.1° to the amount of rise on which the values are calculated. For example, corrections for rises between 2.4 and 2.6 can be taken from the correction based on 2.5°, and corrections for rises between 2.6 and 2.8 taken from the values based on

STEM TEMPERATURE CORRECTION TABLE[1]

Observed rise in temperature = 2.5°

$T - t =$

Initial length of emergent thread N	−4°	−3.5°	−3°	−2.5°	−2°	−1.5°	−1°	−0.5°	−0°
1°	−.0002	.0000	+.0002	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014
1.5°	.0000	+.0002	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016
2°	+.0002	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018
2.5°	+.0004	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020
3°	+.0006	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022
3.5°	+.0008	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024
4°	+.0010	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026
4.5°	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028
5°	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030
5.5°	+.0016	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032
6°	+.0018	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034
6.5°	+.0020	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036
7°	+.0022	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036	+.0038
7.5°	+.0024	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036	+.0038	+.0040
8°	+.0026	+.0028	+.0030	+.0032	+.0034	+.0036	+.0038	+.0040	+.0042

Observed rise in temperature = 2.7°

$T - t =$

N	−4°	−3.5°	−3°	−2.5°	−2°	−1.5°	−1°	−0.5°	−0°
1°	−.0001	−.0001	+.0003	+.0005	+.0007	+.0009	+.0012	+.0014	+.0016
1.5°	+.0001	+.0003	+.0005	+.0007	+.0009	+.0011	+.0014	+.0016	+.0018
2°	+.0003	+.0005	+.0007	+.0009	+.0012	+.0014	+.0016	+.0018	+.0020
2.5°	+.0005	+.0007	+.0009	+.0011	+.0014	+.0016	+.0018	+.0020	+.0022
3°	+.0007	+.0009	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0025
3.5°	+.0009	+.0011	+.0014	+.0016	+.0018	+.0020	+.0022	+.0024	+.0027
4°	+.0012	+.0014	+.0016	+.0018	+.0020	+.0022	+.0025	+.0027	+.0029
4.5°	+.0014	+.0016	+.0018	+.0020	+.0022	+.0025	+.0027	+.0029	+.0031
5°	+.0016	+.0018	+.0020	+.0022	+.0025	+.0027	+.0029	+.0031	+.0033
5.5°	+.0018	+.0020	+.0022	+.0024	+.0027	+.0029	+.0031	+.0033	+.0035
6°	+.0020	+.0022	+.0025	+.0027	+.0029	+.0031	+.0033	+.0035	+.0038
6.5°	+.0022	+.0024	+.0027	+.0029	+.0031	+.0033	+.0035	+.0037	+.0040
7°	+.0025	+.0027	+.0029	+.0031	+.0033	+.0035	+.0038	+.0040	+.0042
7.5°	+.0027	+.0029	+.0031	+.0033	+.0035	+.0037	+.0040	+.0042	+.0044
8°	+.0029	+.0031	+.0033	+.0035	+.0038	+.0040	+.0042	+.0044	+.0046

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[1] T = the initial observed temperature in calorimeter.
t = the observed temperature of emergent stem measured by auxiliary thermometer.

a rise of 2.7° without any appreciable error. As an illustration, suppose the initial temperature of the calorimeter $T = 16.5°$, the temperature of the emergent stem $t = 19°$, the scale reading of the emergent stem = 12° and the observed temperature difference during the determination = 2.8°. Then $N = 16.5 - 12 = 4.5$. $T - t = 16.5 - 19 = -2.5$. From the table, the correction corresponding to initial thread length N of 4.5 and $T - t = -2.5$ and an observed rise of 2.7° is found to be +0.002°. Inspection of the table furthermore shows that in a difference in rise of 2.5 to 2.7 the correction change is only about 0.0002°, hence the additional correction corresponding to the rise of 2.8°, instead of 2.7°, is approximately 0.0001° and can be entirely neglected, which makes the observed correction approximately +0.002.

As may be observed from the table, the amount of the correction varies from practically nothing up to 0.005°. With a water equivalent for the calorimeter of 3,000 cal., this latter amount is equivalent to a correction of 15 cal., a possible correction too large to be omitted if a high standard of accuracy is desired.

For similar working conditions, where the correction was omitted in standardizing the calorimeter with naphthalene, benzoic acid or cane sugar, its omission on determinations made on coal introduces little or no error, as one correction practically balances the other. Unfortunately, similar working conditions day after day cannot be maintained and the stem corrections at different times may vary from less than 0.001 to over 0.004°. The carrying out of the values of other corrections, such as titre and burning of wire fuse, to fractions of a calorie and then omitting this correction entirely is, to say the least, not very consistent practice, and the author believes that the use of a table similar to the one given, whereby the errors can be eliminated regularly, instead of hit or miss, is well worth the little extra trouble which its use involves.

Correction for Variations in the Specific Heat of Water.—Since the specific heat of water is different for different temperatures, exact calorimeter determinations require corrections for determinations made at temperatures other than that at which the water equivalent of the calorimeter was determined. In making this correction, the use of a thermal capacity table for water is a great convenience. Such a table based on Barnes' values for specific heats of water is given by Loeb[1] as follows:

SPECIFIC HEAT AND THERMAL CAPACITY OF WATER FROM 0 TO 50° C.

Temp. °C.	Specific heat	Thermal capacity	Difference	Temp. °C.	Specific heat	Thermal capacity	Difference
0	1.00940	0.00000		25	0.99806	25.05131	
1	1.00855	1.00898	1.00898	26	0.99795	26.04932	0.99801
2	1.00770	2.01710	1.00812	27	0.99784	27.04720	0.99788
3	1.00690	3.02440	1.00730	28	0.99774	28.04499	0.99779
4	1.00610	4.03090	1.00650	29	0.99766	29.04269	0.99770
5	1.00530	5.03660	1.00570	30	0.99759	30.04031	0.99762
6	1.00450	6.04150	1.00490	31	0.99752	31.03786	0.99755
7	1.00390	7.04570	1.00420	32	0.99747	32.03536	0.99750
8	1.00330	8.04930	1.00360	33	0.99742	33.03280	0.99744
9	1.00276	9.05233	1.00303	34	0.99738	34.03020	0.99740
10	1.00230	10.05486	1.00253	35	0.99735	35.02757	0.99737
11	1.00185	11.05694	1.00208	36	0.99733	36.02491	0.99734
12	1.00143	12.05858	1.00164	37	0.99732	37.02224	0.99733
13	1.00100	13.05980	1.00122	38	0.99732	38.01956	0.99732
14	1.00064	14.06062	1.00082	39	0.99733	39.01689	0.99733
15	1.00030	15.06109	1.00047	40	0.99735	40.01422	0.99733
16	1.00000	16.06124	1.00015	41	0.99738	41.01159	0.99737
17	0.99970	17.06109	0.99985	42	0.99743	42.00899	0.99740
18	0.99941	18.06064	0.99955	43	0.99748	43.00644	0.99745
19	0.99918	19.05994	0.99930	44	0.99753	44.00395	0.99751
20	0.99895	20.05900	0.99906	45	0.99760	45.00152	0.99757
21	0.99872	21.05783	0.99883	46	0.99767	45.99916	0.99764
22	0.99853	22.05645	0.99862	47	0.99774	46.99686	0.99770
23	0.99836	23.05490	0.99845	48	0.99781	47.99464	0.99778
24	0.99820	24.05318	0.99828	49	0.99790	48.99250	0.99786
25	0.99806	25.05131	0.99813	50	0.99800	49 99045	0.99795

From this table the differences in the thermal capacity of water throughout the temperature range at which calorimeter work is usually done may easily be calculated and correction made. The correction may be as high as 18 B.t.u. or 10 cal.

With a water equivalent made at usual laboratory temperatures the correction to be applied is usually not large and can be

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[1] *J. Ind. Eng. Chem.* (1911), 175.

neglected in routine work, but for work of the highest accuracy, this correction must be used along with other corrections of similar magnitude, which have been already discussed.

Effect of Hydrogen in the Sample upon Observed Calorific Value.—Any hydrogen in the sample not already combined with oxygen during combustion unites with oxygen to form water, which condenses, and the remaining gas expands as a result of the disappearance of this oxygen. This expansion absorbs heat, the amount absorbed being proportional to the amount of oxygen which disappears. Approximately, 1.36 cal. are absorbed for each 0.01 gram of hydrogen which unites with oxygen. For coals containing 4 per cent of available hydrogen, the correction amounts to about 5½ cal.

The calculation of this effect in brief is as follows: The mechanical equivalent of heat has been determined as 42,350 gram-centimeters = 1 cal. In consideration of gas volumes $\frac{pV}{T}$ is known to be a constant, where V is the volume in gram molecules. Let $p = 1$ atmosphere pressure = 1,033 grams per square centimeter. Let $V = 1$ gram molecular volume of gas = 22.4 liters = 22,400 c.c. Let $T = 273°$ absolute = 0° C. Substituting these values for $\frac{pV}{T} = \frac{1{,}033 \times 22{,}400}{273} = 84{,}750$ gram-centimeters which, expressed in calories = 84,750 ÷ 42,350 = 2 cal. $\frac{pV}{T} = 2$ cal. or $pV = 2T$, which = 546 cal. At 0° C. 2 grams of hydrogen and 760 mm. pressure = 22.4 liters; 0.01 gram of hydrogen = 0.112 liter. The equivalent volume of oxygen uniting with 0.01 gram of hydrogen = 0.056 liter. With $pV = 546$ cal., 22.4 liters = 546 cal., from which 0.056 liter = 1.36 cal. as the amount of heat absorbed as a result of the contraction of the oxygen equivalent to 0.01 gram of hydrogen. Naphthalene ($C_{10}H_8$) contains about 6¼ per cent hydrogen, hence if the heat as burned under conditions of constant pressure is desired, the observed calorific value obtained in the bomb calorimeter should be increased by 6¼ × 1.36 = about 8.5 cal.

The value given for napthalene by the Bureau of Standards is the observed value obtained in a bomb calorimeter, and in using naphthalene as a standard for determining the water equivalent of another calorimeter the observed value is the one that should be used. If, however, the heating value of naphthalene is compared with the heating value of carbon or coal as burned under ordinary conditions, the observed value should be increased by 8.5 cal.

The available hydrogen in coal runs from 2½ to 4½ per cent, which corresponds to corrections of from 4½ to 7 cal. Petroleum contains about 14 per cent hydrogen, which corresponds to a correction of about 20 cal.

The formation of nitric and sulfuric acids during combustion likewise causes a small absorption of heat on account of the oxygen used up. The amount absorbed = 0.58 cal. for 0.01 gram of nitrogen and 0.25 cal. for 0.01 gram of sulfur, and for the amounts of nitrogen and sulfur in coal this can be neglected without any appreciable error.

For the highest grade of work the correction due to hydrogen should be taken into consideration and applied. However, its omission in commercial work cannot cause any very large error.

Use of a Cover on the Water Jacket of the Calorimeter.—A cover on the water jacket is presumably an improvement over the common open-top calorimeter, owing to the smaller radiation changes, but unless used properly a cover may introduce errors larger than the errors that are supposed to be eliminated, and in using a covered calorimeter the author strongly advises beginning the determination at a temperature several degrees below the jacket water temperature so that the temperature of the calorimeter at the end of the combustion period will still be below the temperature of the surrounding jacket water. If this precaution is not observed, a high final rate is very apt to be obtained, due to the surrounding jacket being below the dew point, as compared to the surface of the water in the calorimeter bucket, and a much more rapid evaporation from the surface of the calorimeter water occurs during the final period than at the beginning period when the jacket walls are warmer than the water in the calorimeter.

Impurities in Oxygen.—Compressed oxygen of a high degree of purity for calorimetric work is readily obtained on the market at a comparatively low cost. The author has never found hydrocarbons present in the oxygen in sufficient amounts to affect the calorimeter determination seriously. Their presence, however, is always a possibility and a safe rule which should be strictly followed is to run blanks on naphthalene, benzoic acid or cane sugar on every new tank of oxygen and, if impurities of any consequence are found, they should be corrected for or, better still, the tank should be rejected and a fresh supply of oxygen obtained.

Calculation of Heating Value from Chemical Composition.—Many different formulas have been and are used in calculating the heating value from the chemical analysis. One of the best known and most generally used is Dulong's formula, which is commonly stated as follows:

The heating value = (8,100 × the carbon) + [34,460 × (the hydrogen $- \frac{1}{8}$ the oxygen)] + (2,250 × the sulfur). The results for heating values obtained by the use of this formula are usually within less than 1½ per cent of the actual value as determined in the calorimeter. About 150 analyses of Ohio coals given in Bulletin No. 9 of the Ohio Geological Survey show that the values by Dulong's formula range from about 30 to 100 cal. lower than the value as determined in the calorimeter.

High oxygen coals show a calculated value considerably lower than the determined value, and the calculated values, as a whole, are lower than the determined values.

Some of the differences between the calculated and determined values are very probably due to errors in the determination, while others probably correspond to actual differences in the heat developed by the combustion of the different elements in the combinations in which they exist in the coal. Some organic compounds, such as carbon bisulfide, have a decidedly higher calorific value than the calorific value of equivalent amounts of the elements present. In other words, the decomposition of the carbon bisulfide into its elements liberates heat. Such compounds are known as endothermic compounds. The low results obtained by Dulong's formula on some coals indicate the presence of endothermic compounds in the coal.

CHAPTER XXXIX

THE DETERMINATION OF THE POROSITY AND SPECIFIC GRAVITY OF COKE AND THE SHATTER TEST

The value of coke as a blast-furnace fuel depends somewhat on its porosity, as its speed of combustion will increase with the surface exposed to the blast.

The porosity is usually expressed as the percentage that the volume of the pores forms of the volume of the coke.

It can be determined by weighing the coke in air and then in water, and then filling the pores with water and weighing it again.

The difficulty of filling the pores with water is, however, so great that the results are very uncertain. It requires long boiling in water and repeated exhaustions under an air pump to remove the air; and as there are probably pores which do not open to the surface, the filling is never complete.

The following method, depending on the determination of the true specific gravity of the coke substance and the measurement of the volume of the coke, is much preferable. It is essentially that published by Anderson, W. C., *J. Soc. Chem. Ind.*, **15**, 20.

Determination of the True Specific Gravity of Coke and Coal.—Into the neck of a 50-c.c. specific gravity bottle put a glass tube wide enough to fit air tight when surrounded with a collar made of a rubber tube. The glass tube must have a bulb about an inch in diameter blown in it just above the bottle. It serves to catch and return anything boiling out of the flask. Weigh into this bottle 3.5 grams of the pulverized coke. The coke must be ground in a mortar until it will go through a 40-mesh sieve, and dried at 100°C.

Now add about 20 c.c. of water to the bottle and set it on a water bath for 15 minutes, shaking it occasionally till the coke powder is saturated. Now attach to the tube a Bunsen suction pump giving a good vacuum and exhaust the air till the liquid boils gently. Continue the boiling in a vacuum for two and one-half hours. Remove the flask, cool it, fill it up with water and weigh as usual after inserting the stopper.

The bottle should have a counterpoise, of course, so that the weight obtained will be that of the coke and the water only. As the bottle holds exactly 50 grams of water, the specific gravity of the coke will be

$$\frac{W}{W-(W'-50)}.$$

DETERMINATION OF THE APPARENT SPECIFIC GRAVITY OF COKE

The apparatus used for the determination of the apparent specific gravity consists of a galvanized iron can about 15 in. in diameter and 2 ft. high, nearly full of water; a heavy wire basket, 9 in. in diameter and 12 in. high, provided with a wire cover and a wire bale or handle; a beam balance supported upon a bracket projecting from the wall; and a hook with which the basket may be suspended from the balance while weighing. The balance should be graduated to 50 lb. in 1/10 lb.

The method of determining the apparent specific gravity is as follows: The basket is weighed in the air empty, then filled with lump coke in the form of 1½- to 2-in. cubes, and again weighed. The difference in weight in air of the basket filled with coke and the empty basket is the weight of coke used. The basket of coke is immersed in the can of water, moved up and down several times to remove the air bubbles, hooked to the balance and weighed, keeping the basket of coke completely immersed in the water. The basket of coke is taken out of the water, the coke removed from it and the empty basket is weighed in the water. The difference in weight of the basket filled with coke and the empty basket, both in water, is the weight of the coke sample in water.

If the weight of the sample in air $= x$, and the weight of the sample in water $= y$, the apparent specific gravity $= \frac{x}{x-y}$.

In making the apparent specific gravity determination of coke, the sample should be thoroughly dried before starting, and preferably in the form of 1½- to 2-in. cubes. Since the pores in coke are large, the sample takes up water rapidly, and it should not, therefore, be allowed to remain in contact with the water more than five minutes during the determination.

SHATTER TEST

Shatter Test Machine.—The shatter test machine consists of a box 18 in. wide, 28 in. long and approximately 15 in. deep, supported above a

½-in. rigidly mounted steel plate. The inside of the bottom of the box is 6 ft. above the plate. The bottom of the box consists of two doors hinged lengthwise and latched so that they will swing open freely and not impede the fall of the coke. Steel plates about 8 in. high are placed around the plate so that no coke may be lost. To prevent breakage of any coke that may result in placing the sample in the box, it should be so constructed as to permit lowering it to a convenient level. In it, two pulleys attached to the top of the frame make it possible to support the box at the levels desired by means of counterweights and ropes.

Screens.—For determining the coke breakage, square mesh screens with the following openings are used: 2, 1½, 1 and ½ in.

Collection of Sample at the Source.—If the shatter test is to be used to indicate the probable breakage of coke on handling, the sample should be taken before it is subjected to breakage resulting from screening and loading into cars.

By-product Coke.—In the case of by-product coke the sample should be collected from the coke wharf or quencher car. Approximately 75 lb. of representative coke pieces, none of which in any position pass a 2-in. square mesh screen, are selected from the coke wharf for each individual test. This is best accomplished by dividing the coke on the wharf into imaginary equal areas and selecting an equal number of pieces from each area. Each coke piece selected should be approximately equal in length to one-half the width of the coke oven, and each end should show the configurations characteristic of a full-length piece—a cauliflower end produced at the wall of the oven and a parting end produced at the center of the oven.

Beehive Coke.—At beehive works, samples for the shatter test are collected as the coke is being drawn from the ovens by selecting five full-length pieces of coke from each oven, in accordance with the plan already described for sampling coke from beehive ovens. Each piece should be as uniform in thickness as possible, so as to represent the true proportion of top, middle and bottom coke.

Collection of Sample at Place of Delivery.—The sample is best collected as the coke is delivered from the cars into the bins. This may be accomplished by placing a scoop of approximately 10 lb. capacity, at regular intervals, in the coke stream during the period of unloading. The sample collected should be of sufficient quantity to give approximately 75 lb. of coke pieces, none of which pass a 2-in. square mesh screen.

It is very difficult to collect a representative sample from coke exposed in bins and coke cars. If the collection must be made in this way, care should be taken to select pieces which will represent the entire exposed area. To this end, the exposed surface to be sampled is best divided into imaginary equal areas, and an equal number of pieces is selected from each area. Approximately 75 lb. of representative coke pieces, none of which will pass, in any position, through a 2-in. square mesh sieve, are to be collected.

Method of Making the Test.—Approximately 50 lb. of the sample are placed in the box of the coke shatter test machine, the coke is leveled, the box is raised and the coke is dropped upon the plate. The box is lowered to a convenient height for transferring the sample into it, in order to prevent breakage of the coke, and the sample, including all the shatterings, is replaced therein. These operations are repeated until the sample has been dropped four times upon the plate. After the fourth drop, the material is screened successively on the 2-, the 1½-, the 1- and the ½-in. square meshed screens.

Care should be taken in screening to prevent breakage of the coke pieces. The coke is screened in such increments as to allow all pieces to be in direct contact with the meshes. The coke remaining on each screen and that passing through are weighed separately. If the sum of these weights shows a loss of over 1 per cent, the test is rejected and another made.

The shatter test is reported as the percentage on and through each screen. Since the average probable error in a single shatter test determination is approximately 2 per cent, it is advisable to make several determinations and report the average results.

CHAPTER XL

DETERMINATION OF YIELDS OF COKE AND BY-PRODUCTS FROM BITUMINOUS COAL AND OF THE RESULTS OF WASHING COAL

The reactions of the coal substances under the influence of heat vary with conditions. Therefore, yields of coke, gas and by-products obtained from coal by any distillation process are to be considered as relative only. Since it is practically impossible to conduct tests in the laboratory under the same conditions of time, temperature and mass which prevail in the regular operation of the coke plant, the conditions of the test are standardized to give the maximum yields. Then, by frequent comparisons of the laboratory results with those obtained in actual practice, a certain correlation is revealed between the laboratory and the plant results, and, by applying this relation as a correction to the results obtained from the laboratory test, the coke, gas and by-product yields of any given coal for that plant can be fairly accurately estimated. For a detailed description of the method, see "Sampling and Analysis of Coal, Coke and By-products" by Chemists of the United States Steel Corporation.

It has been shown by White in Bulletin 29, U. S. Geological Survey, that the probable coking value of a coal may be estimated by a comparison of its hydrogen-oxygen ratio with that of the known coking coals. A rough determination of the analysis of a coke obtained from a coal may be made as follows:

In order to obtain the analysis of the coke produced from a coal, it is necessary to prepare a sample of the coke. This can be done in a small wind furnace as follows: Select two clay crucibles of such a size that one will set easily inside of the other. The writer uses a Denver fire-clay, "20-gram assay" crucible for the inner and a large "Hessian" for the outer. Grind a cover onto the inner one with sand until it fits closely. Put the larger one in the furnace and let it get bright red-hot. Meanwhile charge the smaller with 100 grams of the coal, crushed to about ¼-in. mesh. Cover the smaller crucible and set it in the large one, throw a little coal in on top of it, and then carefully cover the larger one. At the end of an hour take out both, put a little more coal into the outer crucible, and then let them cool while covered. When cool, take out the inner crucible and remove the coke from it. The object of the coal in the outer crucible is to prevent oxygen from getting into the coke and burning out sulfur.

TESTING THE EFFECT OF "WASHING" ON COAL

The object of the washing of coal on jigs or tables or pneumatic cleaners or other washers is the reduction of the ash and the sulfur in the coal. The benefit that a given coal will receive in the process will depend upon the form in which these impurities occur in it. Only the ash which is due to intermixed slate and the sulfur which is in the form of free pyrite can be removed by the process, which depends upon the difference in the specific gravity between these materials and the coal. The fineness to which the coal must be crushed in order to effect a satisfactory breaking apart of the heavy and light material will depend upon the nature of the coal seam. The finer the coal has to be crushed, the greater will be the loss of coal in the slimes. All these points can be investigated in the laboratory.

The operation consists in crushing the coal to some determined maximum size, then separating it into a series of sizes by sieves, and finally separating these sizes into their heavy and light components.

The specific gravity of bitumenous coal is less than 1.35, while that of the impurities is always above this figure; hence, the separation into light and heavy parts can be made, as suggested by Dr. Drown, by mixing the coal with a solution of $CaCl_2$, of 1.35 sp. gr., in which the coal will float and in which the impurities will sink. Anthracite is much denser and a $ZnCl_2$ solution of about 1.66 sp. gr. must be used.

Before carrying out the final washing the proper sp. gr. of the solution to be used should be determined by preliminary tests of the sp. gr. of the pure coal and the impure coal.

The apparatus needed consists of, first, a set of sieves of 1-in. to 1/200-in. mesh; second, a "glass tank," or some equivalent, in which a small quantity of material can be washed; third, a solution of calcium chloride of about 1.35 sp. gr., made by dissolving

1 lb. of crude $CaCl_2$ in a pint of water, and, when the solution has cooled, diluting it to exactly the right gravity.

The coal is crushed, avoiding the production of dust as far as possible, until it will all pass through the half-inch sieve. The sample is then thoroughly mixed and a weighed amount of it (from 3 to 5 kg.) sifted over the ½- to 1⁄200-in. sieves. This divides it up into sizes ½ to ⅜, ⅜ to ¼, ¼ to ⅛, ⅛ to 1⁄16, 1⁄16 to 1⁄32, 1⁄32 to 1⁄64, etc. The quantity in each size is then weighed and expressed in percentages of the whole. The various sizes are now treated separately in the chloride of calcium solution as follows: A glass tank holding about a gallon is nearly filled with the solution, the coal put into it a little at a time and well stirred to wet it thoroughly and detach all air bubbles. The coal rises to the surface, while the slate and pyrite settle to the bottom. Enough of the coal should be put in at a time to make a layer about an inch thick when it rises to the top. This is now skimmed out with a little dish or a dipper and dropped into a large funnel, the neck of which is closed with a wad of glass wool. More coal is now added to the solution and the operation continued until all of the given size is thus separated. The coal in the funnel is then thoroughly cleaned from chloride of calcium by repeatedly pouring water over it, allowed to drain, then spread out on paper, air dried and weighed. The chloride of calcium solution is then carefully poured off from the heavy material in the tank, which is then washed out, filtered dried and weighed. Each of the above products should then be analyzed for ash and sulfur. As a check, the analysis of the original coal should be computed from the analysis of these products and should agree very closely with that of the original sample.

A little practice is necessary in order to manipulate the separation properly. From a comparison of the results shown on the various sizes, it may be desirable to repeat the experiment, crushing the whole of the coal ¼ in. or even to ⅛ in. in order to separate very finely disseminated pyrite and secure a coal low in sulfur. But as the loss in washing falls almost wholly on the finer coal, the increase of the proportion passing the smallest sieve must be carefully noted.

When many tests have to be made it is well to use the "Delatester" made by the Tyler Co.

REFERENCES: See DROWN, *Trans.* Am. Inst. Min. Eng., **13,** 341. STOEK, *J. Soc. Chem. Ind.* (1897), 304.

CHAPTER XLI

THE ANALYSIS OF GASES

The analysis of gases is comparatively simple in theory, but no branch of analytical chemistry requires more skill and experience for accurate results. Very careful attention to detail of manipulation, both in sampling and in analysis, is necessary if the results are to be really dependable.

The methods of gas analysis may be classified as: First, those based upon volume changes; second, titrimetric; third, gravimetric. Most determinations belong to the first class, that is, they are based upon measurement of the decrease in volume of a gas mixture when some constituent is removed by chemical or physical methods.

The gas mixtures which the metallurgical chemist is likely to be called upon to analyze are tabulated below with their approximate compositions. Of course, these compositions are merely typical.

	Chimney gas, per cent	Blast-furnace gas, per cent	Producer gas, per cent	Natural gas, per cent	Coke-oven gas, per cent	Retort gas, per cent	Water gas, per cent
CO_2	8.6	13.5	6.3	0.2	2.0	2.1	3.5
C_2H_4	....	....	0.6	......	1.9	3.8	
O_2	10.3	0.0	0.0	......	0.3	0.5	0.6
CO	0.2	25.5	23.7	......	6.4	8.0	43.5
H_2	....	3.0	11.1	......	56.3	47.8	47.3
CH_4	....	0.2	2.6	85.3	19.0	26.4	0.7
C_2H_6	....	....	....	12.5	2.0	2.0	
N_2	80.9	57.8	55.7	2.0	12.1	9.4	4.4
B.t.u.	....	94.5	149.0	1168.0	460.0	545.0	302.0

Besides the gas constituents given in the above table, the gas chemist is required frequently to determine the amounts of H_2O, H_2S, CS_2, "light oils" (C_6H_6, C_7H_8, C_8H_{10}), naphthalene ($C_{10}H_8$), cyanogen (CN), SO_2, NH_3, oxides of nitrogen and, at smelters, the constituents of fume in gas, such as As_2O_3, PbO, ZnO, etc. Perhaps the most difficult determination of all is that of the dust in blast-furnace gas.

Mine air, which requires many analyses, is simply air in which part of the oxygen has been absorbed by coal and to which has been added various small amounts of CH_4, CO_2 and, in case of mine fires, CO and other hydrocarbons which may be present.

Sampling.—The sampling of gases as they are found in the mains, gas producers and furnaces about metallurgical plants is sometimes a very simple matter and sometimes very difficult. For instance, the sampling of gas in a gas main, a considerable distance from the source of the gas, may be merely a matter of taking gas out of the gas-cock, but the sampling of gas in the hearth of a blast-furnace or at the exit of an open-hearth steel furnace or even in the flues leading from steam boilers is sometimes very difficult, that is, it is very difficult to get an accurate sample. The diversity of conditions under which it may be necessary to take gas samples makes it impossible to give directions here other than sufficient to illustrate the general principles.

In the sampling of gases two kinds of samples are recognized—the accumulative or "long-time" sample and the control sample. The accumulative sample is one which is taken continuously through the entire period of an operation running from one-half of an hour to 24 hours. For instance, in operating a gas retort, the composition of the gas derived from the coal in the retort varies continually from the beginning to the end of the carbonization, both in quantity and composition. A gas sample, truly to represent the average composition of the gas given off during the entire period, would have to be taken continually at a constantly varying rate bearing constant ratio to the rate of gas making. This is best done by a proportioning meter.

Control samples are those taken in a short period of time and which represent the gas merely for that short period of time, sometimes only a few seconds. All reports should, of course, state the way the sample was taken.

Sampling Flue Gas.—The gas should be drawn from the flue by a pipe that crosses it at right angles and extends to within 6 in. of the further wall. The end of the tube should be closed with a cap, and the gas should be drawn into it through a number of holes about $\frac{1}{16}$ in. in diameter, drilled along the side of the tube at regular intervals not greater than 6 in. The nearest holes should not be less than 6 in. from the side of the flue. The diameter of the tube should be at least 12 times the diameter of the holes in the side. This will insure a uniform sampling across the flue.

Professor Lord carefully tested this point by inserting such a tube in air and gas for different portions of its length and analyzing the gas drawn from the tube. The composition of the issuing mixture was always proportional to the number of holes in the gas and in the air, air and gas being under atmospheric pressure.

The sampling tube can be made of iron, if the temperature of the flue does not exceed 340°C., as at that temperature iron, even if rusted or covered with soot, is without action on flue gas, neither the CO nor the CO_2 being affected. This point was tested by the writer by passing flue gas containing CO through a glass tube filled with iron tacks, also with rusted tacks and with soot and tacks. The tube was immersed in a bath of melted lead and the temperature of the lead measured by a nitrogen-filled high-temperature thermometer. If soot and rust are present on the iron, action begins about 340°C., and is rapid at 400°C., CO being oxidized by the Fe_2O_3 and oxygen consumed by the soot, forming CO_2. With clean iron, however, there is practically no action at 400°C. As 340°C. is above the temperature at which most flue or blast-furnace gas is drawn off, the use of iron tubes is generally permissible. For flue temperature higher than 340°C., water-cooled tubes must be used for withdrawing the samples. For rapidly withdrawing a single sample from the interior of a furnace, an iron tube, open at the end and wrapped with ¼ in. of sheet asbestos tied on with wire, can be used. The asbestos cover is well soaked with water and the tube run into the furnace and the sample drawn. A tube so protected can remain in a white-hot furnace for two or three minutes without the asbestos drying or the tube heating beyond a safe point. A silica tube is convenient for sampling gases from a very hot place, such as at the ports of an open-hearth furnace. Where there is a strong draft, as in a chimney flue, it is important that the opening by which the tube passes through the wall be well plastered up with clay, or air may be drawn in and reach the nearer holes and affect the sample. From the end of the sampling tube the gas is drawn continuously by a water or steam aspirator. If the gas sample is to be kept any time before analysis, it must be borne in mind that gases containing CO_2 cannot be preserved over water, as the CO_2 is rapidly absorbed. If confined over water, the water should be covered

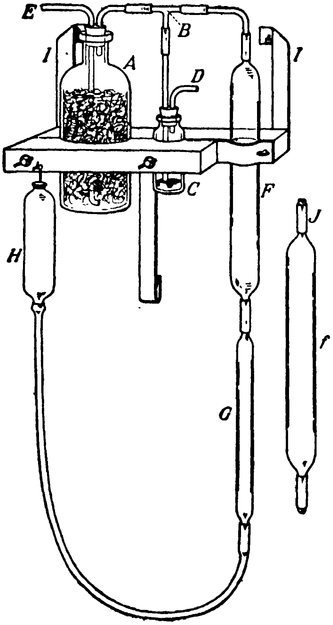

FIG. 20.

with paraffin shavings. The writer has found that if the water be well covered with paraffin shavings a sample of gas with 10 per cent CO_2 will not lose 0.10 per cent CO_2 in three hours.

In most cases it is possible and far preferable to make the analysis at the furnace, especially where a series of analyses is required. Where this is not possible, as, for instance, on a locomotive engine test, the apparatus shown in Fig. 20 will be found very effective and convenient for drawing a series of samples at short intervals.

The sample tube *F*, *f* has a capacity of about 250 c.c.; the ends are closed with rubber tubes stopped with short glass rods *J*. A number of these sample tubes are provided; they are kept in a rack in a box, and are filled with water before starting out. In the apparatus itself, *A* is a bottle of about a liter capacity, containing absorbent cotton to filter the gas. *C* is a small bottle containing a little mercury; it serves as a trap to prevent reversal of the gas current. The gas enters through *E*, and is drawn out through *D* by an aspirator at the rate of about 150 c.c. a minute.

Thus the bottle *A* will always contain a gas representing the average of several minutes. *H* is a "pressure bottle," connected as shown.

In taking the sample, the apparatus is set up as shown; the gas is supposed to be flowing freely through the bottles *A* and *D*. A pinch-cock (not shown) on the rubber connection between the Y-tube and the sample tube is opened and gas drawn in by lowering the pressure bottle *H* until the gas fills the tube and also the lower tube *G*. The cock is then closed and the pressure bottle lifted, so as to put the confined gas under a little pressure; but the lower tube *G* must contain gas enough to prevent any water getting into the sample tube. The rubber connection with *F* is now pinched tight and the tube disconnected. It is then closed by inserting the glass rod into the rubber. The lower end is closed in the same way. The rubber tubes and stoppers on the sampling tube can be wired if necessary to keep them tight. As the gas is under a little pressure, any leakage during the disconnection will be out from and not into the gas.

The tube is now replaced by a second one and the apparatus is ready for drawing a new sample.

Fig. 20*a* shows a convenient arrangement for drawing a single sample rapidly, as, for example, through an asbestos-covered pipe such as was described.

The bottle *C* contains a little mercury and serves as a trap. The bottles *A* and *B* contain brine covered with paraffin shavings *P*. The gas delivery tube is connected with the tube *F*. *B* is filled with water by raising *A*, the air escaping through the mercury in *C*. Now *A* is lowered and the gas drawn in through *F*, the mercury preventing any return through *E*. In this way the gas can be drawn and emptied till all air is expelled, and then the bottle *B* filled and the pinch-cock *D* closed and the sampler removed. The bottles may be of large capacity so that the sample may be taken over many minutes. The water in *B* should be shaken with some of the gas in order to become saturated with it.

If it is desired to draw a sample continuously for several hours, the apparatus shown in Fig. 21 can be used. It will draw a sample at a nearly fixed rate per minute for several hours. It should be filled with similar gas for some days and then emptied before use, as a new metal gas holder affects the sample a little at first.

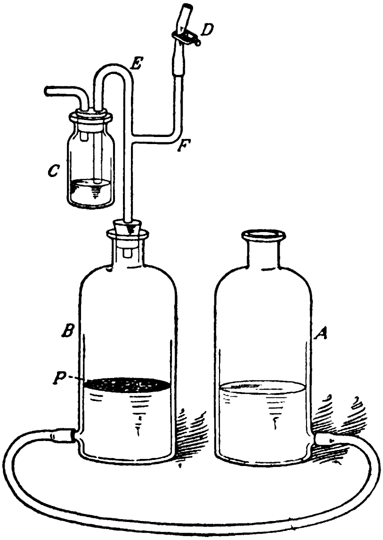

FIG. 20*a*.

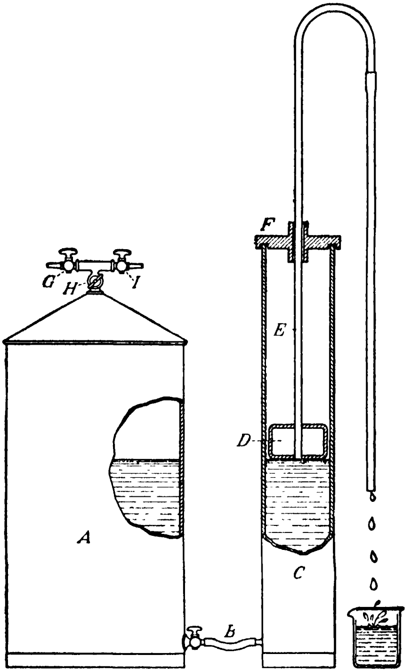

FIG. 21.

The gas is drawn into the tank *A* through the cock *G* by the escape of the water at the bottom through the tube *B*. The rate of this escape is kept uniform by the floating siphon *E* in the connecting cylinder *C*. The tube *B* is large, so that the level of the water in the tank and the cylinder is the same, and the rate of flow from the latter is regulated by the constant head of the floating siphon carried by the float *D*.

In analyzing the flue gas on boiler tests, one sample should be taken every 30 minutes. This will give a fairly accurate average for the period of 10 hours usually covered by the test. Experiments made by F. Hass in the Department of Metallurgy, Ohio State University, showed practically no difference in the results obtained by averaging samples taken every 30 minutes and every 15 minutes for 10 hours. Samples taken in the continuous sampler above described always show less CO_2, but otherwise agree closely with the average of the half-hour samples covering the same 10 hours, provided they are analyzed promptly. If the sample in the tank is allowed to stand for some time, the loss of CO_2 with a corresponding increase of nitrogen and oxygen may be very marked. The following two analyses illustrate the comparison for a 10-hour test. It shows the loss of CO_2.

	Average of 30-minute samples	Gas from tank
CO_2	11.1	10.4
O_2	8.0	8.25
CO	0.43	0.30
N_2	80.47	81.05

When such a long-time sample is taken over water, it is necessary to take a number of instantaneous samples and analyze them for CO_2 only, as this is the constituent most soluble in water, and make correction when the long-time sample is analyzed for the CO_2 absorbed in the water. This is also true when H_2S or SO_2 are important constituents of the gas.

In sampling gases the following points must be kept in mind:

1. The gas may contain constituents soluble in water.
2. The gas may undergo change in passing through a hot iron tube, especially if oxidized.
3. The gas in the flue or passage from which the sample is taken may be stratified and quite non-homogeneous and, hence, it is necessary to use a sampling tube which will take gas in proper proportion across the entire diameter of the flue or port.
4. If the gas stream contains dust or liquid vesicles, such as tar, these constituents will settle in a horizontal flue so that the gas near the bottom will be higher in dust and tar mist than near the top.
5. Gas samples when stored in glass vessels will undergo change if the glass walls are wet and alkaline.
6. Hydrogen is a constituent of many gases, such as coal gas or water gas, and its diffusibility through thin rubber tubes is quite great.

Gas sampling tubes with glass stop-cocks are unreliable for the storage of samples for any considerable length of time. We have found that by far the most satisfactory way of handling and storing samples is in ordinary 500-c.c. small-mouthed bottles, closed with a rubber stopper, and with just enough water to cover the stopper when the bottle is inverted. In the case of highly important samples, mercury should be used for covering the stopper instead of water. The bottle with the gas sample in it should always be kept inverted.

When long-time samples are taken and the sample is large in volume, making necessary the use of a large gas holder, the gas, of necessity, is in contact with water a long time. To decrease the solubility of the gas, a strong brine solution is useful, though this only minimizes the errors. The containing liquid should be previously saturated as near as possible with the kind of gas that is to be sampled. Even then it is quite essential to take a number of short-time samples in bottles and analyze them for the constituents highly soluble in water.

The solubility of some of the gases in water are given in the following table. The values are for a pressure of 760 mms. of the gas when in equilibrium with water, and are expressed as the number of cubic centimeters of the gas which dissolve in 1 c.c. of water at 15°C.

Ammonia	802.0000	Nitrogen	0.0179
Argon	0.0400	Nitrous oxide	0.7400
Carbon dioxide	1.0190	Oxygen	0.0340
Carbon monoxide	0.0250	Hydrogen sulfide	3.5200
Chlorine	2.6300	Sulfur dioxide	56.6000
Helium	0.0139	Methane	0.0390
Hydrogen	0.0190	Ethylene	0.1470
Hydrochloric acid	458.0000		

The values for chlorine, hydrochloric acid and sulfur dioxide are for a total pressure of the gas and water vapor equal to 760 mms.

Reactions and Reagents Used.—Carbon dioxide is rapidly and completely absorbed by NaOH or KOH solutions. The reaction is $CO_2 + 2NaOH = Na_2CO_3 + H_2O$. Sulfur dioxide, hydrogen sulfide, oxides of nitrogen and any acid gases are similarly absorbed. Also, a gas which is high in unsaturated hydrocarbons and in the benzene hydrocarbons loses some of these constituents by absorption in the caustic. Hence, the solution should be thoroughly shaken up with some of the gas before the regular sample is taken for analysis.

Ethylene and similar members of the olefin series are rapidly absorbed by fuming sulfuric acid (sulfuric acid containing an excess of SO_3), according to the reaction, $C_2H_4 + 2H_2SO_4 = C_2H_6S_2O_7 + H_2O$. The uming sulfuric acid also absorbs acetylene, forming $C_2H_4SO_4$, and the hydrocarbons of the benzene series, forming benzene sulfonic acid, $C_6H_5SO_3H$, and similar derivatives. The higher hydrocarbons of the paraffin series, such as C_5H_{12} and C_6H_{14} (gasoline hydrocarbons), are absorbed in the acid. Too prolonged contact will cause the absorption of small amounts of even methane and ethane. A time of contact of less than five minutes will cause no measurable absorption. The hydrocarbons above mentioned also react with free bromine, forming bromides, such as $C_2H_4Br_2$.

Oxygen is absorbed by alkaline pyrogallate solution or by phosphorus. The pyrogallate solution is most convenient for technical work, in that it is easily prepared, is not poisoned by certain gases, is not affected by light, and absorbs oxygen rapidly at any concentration. The potassium solution absorbs oxygen rapidly, is of a lighter color and does not clog the capillary tubes as rapidly as the sodium solution.

Phosphorus pipettes have the advantage of requiring much less frequent recharging than pyrogallate pipettes. It absorbs oxygen rapidly by simple contact. The formation of white clouds indicates the presence of oxygen, and their disappearance shows that the absorption is complete. A temperature of 15 to 20°C. is best suited for the absorption. At lower temperatures the reaction is very slow. The reaction does not proceed if the gas contains more than 50 per cent oxygen. Oxygen is not absorbed if the gas contains traces of unsaturated hydrocarbons, ethereal oils, alcohol, ammonia, phosphine or sulfur compounds. There is, however, easy ocular evidence of the reaction, so that there need be no uncertainty as to whether the reaction has taken place. When once started it goes to completion. When a gas containing oxygen is introduced into a phosphorus pipette, there normally appears at once a dense white cloud of oxides of phosphorus, which are evident even when the amount of oxygen is less than 0.1 per cent of the total volume. All technical gases will contain this much oxygen, for even if they did not contain it originally, they will have absorbed it from the water of the sampling apparatus or of the burette, so that the presence of these clouds is a sure indication that the reaction is progressing properly. The absence of any smoke does not mean that there is no oxygen present, but that there is something preventing the reaction. The danger of fire and burns in using phosphorus is a serious disadvantage. Oxygen combines with phosphorus to phosphorus trioxide.

Potassium pyrogallate has the formula $C_6H_3(OH)_3$ and, like all the polyhydric phenols, is easily oxidized, thus making it a good reagent for, oxygen. It is essential that the reagent be made up as directed, since, when not of proper strength, the reaction with oxygen causes the liberation of a small amount of carbon monoxide which will make the results wrong for carbon monoxide as well as for oxygen.

Carbon monoxide is absorbed by either acid or alkaline ammoniacal cuprous chloride, according to the reversible reaction $Cu_2Cl_2+2CO \leftrightarrows Cu_2Cl_2.2CO$. The compound is quite unstable and complete absorption is only possible with fresh solutions. It is, therefore, necessary to use at least two cuprous chloride pipettes when the amount of CO in the gas is large, the greater part of the CO being absorbed in the first pipette and the small remainder being absorbed in a solution practically free from CO. Oxygen and the unsaturated hydrocarbons are absorbed in the cuprous chloride solution, hence they must be removed before the cuprous chloride is removed. It is preferable to use the alkaline solution, as the ammonia vapors are rapidly absorbed in the dilute acid solution used in the measuring burette, and hence do not cause error.

Hydrogen may be absorbed by palladium sponge but the palladium must be regenerated after each test. It is more satisfactorily absorbed by a solution of palladous chloride, as directed by CAMPBELL and HART (*Am. Chem. J.*, **18**, 294). The solution is prepared by dissolving 5 grams of palladium in 30 c.c. of HCl, containing 2 c.c. of HNO_3, evaporating just to dryness, dissolving in 5 c.c. of HCl and diluting to 750 c.c. The solution is used in a single pipette which must be heated to 50°C. Hydrogen is more usually and conveniently determined by combustion with oxygen in the presence of palladiumized asbestos at a temperature of 100°C. or by oxidation with copper oxide at 300°C.

Methane and ethane are determined together by combustion with oxygen in contact with a platinum spiral heated to a bright yellow, or by oxidation with copper oxide at a bright red temperature. They are then calculated from the combustion data. They may be determined by explosion and calculated from the volume change and CO_2 produced, but the writer does not like this method and has ceased using it.

Hydrogen sulfide is determined by titration with standard iodine solution, CS_2 by combustion after the hydrogen sulfide is removed and the sulfur is oxidized to SO_3 and precipitated as $BaSO_4$.

The benzene hydrocarbons are determined by absorption in an absorbent oil and afterward distilling them and measuring their amounts.

Naphthalene is determined by absorption in a standard picric acid solution and titrating the excess of acid.

Ammonia is determined by absorption in a standard HCl solution and titrating the excess of acid.

Cyanogen is determined by absorption in a strongly alkaline solution of ferrous sulfate and titration of the ferrocyanide so formed by standard zinc sulfate.

Preparation of the Reagents.—KOH solution. Dissolve 100 grams of the best quality potassium hydroxide in 300 grams of water. Let the solution stand in a closed bottle till any oxide of iron settles, and use only the clear solution. It is best to prepare a quantity of this and keep it some time before use. Carbon dioxide is easily and rapidly absorbed in the KOH, forming K_2CO_3.

Potassium Pyrogallate.—This is the best absorbent for oxygen. Phosphorus is also frequently used, but it is too easily "poisoned," so that it will not work. The writer always prefers the pyrogallate. It is made by dissolving 15 grams of pyrogallic acid, $C_6H_3(OH)_3$, in 100 c.c. of a solution of KOH (sp. gr. 1.55). The solution will absorb about 20 c.c. of oxygen per cubic centimeter.[1] It acts rapidly at first but as it becomes saturated with oxygen it acts more slowly. The relation of the pyrogallic acid to the alkali is important, for, if the concentration of alkali is too low, some CO may be given off when oxygen is absorbed. The solution as above made will not evolve CO. At temperatures above 15°C. the absorption is rapid, the oxygen in 100 c.c. of air being absorbed in three minutes, but at lower temperatures the absorption is much slower. Of course CO_2 will be absorbed in this solution and it must be previously removed with KOH. If the gas contains only a little oxygen the pyrogallate solution is best made by dissolving 15 grams of pyrogallic acid in 150 c.c. of 30 per cent KOH.

Ammoniacal Cuprous Chloride.—Dissolve 450 grams of ammonium chloride and 400 grams of cuprous chloride in 1,500 c.c. of water. For use, the solution is diluted with one-third its volume of ammonia water (sp. gr. 0.9). Some metallic copper should be kept in the solution to keep it active. One cubic centimeter will absorb about 16 c.c. of CO. The reaction is $2CuCl + 2CO = Cu_2Cl_22CO$. However, this compound is very unstable and, after a certain amount of it has been formed in the solution, it begins to decompose and to give up CO. Consequently, in all work where much accuracy is required, it is absolutely necessary that the greater part of the CO be first absorbed in one cuprous chloride pipette and then the remaining CO be absorbed in a pipette containing freshly prepared cuprous

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[1] Anderson, *J. Ind. Eng. Chem.*, **7**, 587.

chloride solution. The second one, after it has been used a number of times, is made the first and a fresh supply is put in the second.

The cuprous chloride also absorbs oxygen, hence the oxygen in the sample must be removed before the CO is absorbed in the cuprous chloride. Cuprous chloride will also absorb acetylene, ethylene, etc.

The cuprous solution may be regenerated by heating in a flask with strips of copper and with a reflux condenser for several hours. The CO is eliminated. More ammonia must be added after the heating.

Stick Phosphorus.—This reagent is obtainable in sticks $\frac{3}{16}$ in. in diameter. It may also be prepared from larger sticks by melting the phosphorus under water in a test-tube immersed in a vessel of water at a temperature of about 50°C. A glass tube of the proper internal diameter is inserted in the molten phosphorus, and a column of phosphorus is drawn into the tube by means of suction to the desired height, when the tube is withdrawn and immediately dipped into a beaker of cold water. The solidified phosphorus is then pushed out with a glass rod into the reagent pipette, also filled with water. Extreme care must be taken to avoid spilling the phosphorus on the floor. When in use, the water in the pipette is renewed occasionally to remove the oxides of phosphorus in solution. The need for this removal is indicated when the fumes in the pipette are slowly or incompletely absorbed in one or two minutes. The chamber of the pipette containing the phosphorus is enclosed with a piece of black paper to protect it from the action of light.

Fuming Sulfuric Acid.—Two hundred sixty cubic centimeters are required. The acid should contain at least 20 per cent of the sulfur trioxide in excess. It will become discolored, owing to its action upon the rubber tubing, but this does not appear to interfere with its efficiency. This action tends to harden the tubing, and then apparently ceases.

General Principles.—All perfect gases, according to Avogadro's law, contain the same number of molecules of the gas per unit volume at the same temperature and pressure. It follows, therefore, that the gram molecular weights of all gases occupy the same volume. This volume is 22.41 liters at 0°C. and 760 mm. pressure. Hydrogen, nitrogen, oxygen and carbon monoxide are nearly perfect gases. Carbon dioxide departs considerably from being a perfect gas at ordinary pressures, and the same is true of ethane. The ratios of theoretical to observed densities of a number of gases are given in the following table:

Gas	Molecular weight	Specific gravity (Air = 1)		Observer	Theoretical / Observed
		Theoretical	Observed		
CH_4....	16.03	0.5538	0.5545	Baumé and Perrot....	0.999
C_2H_6....	30.05	1.0381	1.0494	Baumé and Perrot....	0.990
CO.....	28.00	0.9673	0.9670	Leduc...............	1.000
CO.....	28.00	0.9673	0.9672	Rayleigh............	1.000
CO_2.....	44.00	1.5201	1.5287	Leduc...............	0.994
CO_2.....	44.00	1.5201	1.5291	Rayleigh............	0.994
N_2......	28.02	0.9680	0.9674	Rayleigh............	1.001
N_2......	28.02	0.9680	0.9672	Leduc...............	1.001
O_2......	32.00	1.1055	1.1054	Rayleigh............	1.000
O_2......	32.00	1.1055	1.1052	Leduc...............	1.000
C_2H_4....	28.03	0.9683	0.9852	Saussure............	0.983
C_2H_2....	26.02	0.8989	0.9056	Leduc...............	0.992

At lower partial pressures the departures from the condition of a perfect gas are less, for instance, at a pressure of 100 mm., the factor for carbon dioxide is 0.999.

The equation for perfect gases, which expresses the relation between pressure, volume and temperature, is $PV=RT$, where P is pressure, V is volume, T is temperature (absolute) and R is a constant. This equation is modified for gases which are not perfect gases by Van der Waals's equation expressed thus:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT,$$

in which a is a constant which refers to the molecular attraction of the gas molecule and b is a correction factor for the volume occupied by the molecule.

The basis for the calculation and reporting of gas volumes in the engineering world of this country is not 0°C. and 760 mm. pressure of dry gas as given above, but is 60°F., 30 in. of mercury pressure and saturated with water, and the pound is the unit of weight. One pound molecular volume of any perfect gas, when saturated with water, occupies 386 cu. ft. at 60°F., 30 in. of mercury pressure. Of course, the same correction factors given in the above table are used for gases which depart from the condition of ideal gas.

Gases are practically always analyzed in apparatus containing water and are, therefore, saturated with water. The results obtained by gas analysis methods are correct, however, for the composition of the gas on the dry basis, not on the wet basis, because when a given constituent is absorbed, the water vapor corresponding to the amount of the constituent absorbed at the same time condenses, since with constant temperature the aqueous tension in the remaining gas remains constant.

Further, if the gas contains tar or heavy hydrocarbon vapors in the hot main, these will condense more or less completely when the sample is taken and will not be obtained in the analysis. They must be determined by special methods.

Any change in the temperature of the gas during analysis will produce error in two ways, first, according to the law that the volume of a gas is proportional to its absolute temperature; second, because of the fact that any change in temperature will change the aqueous tension in a gas standing over water. Thus, if 100 c.c. of gas at 20°C. and 745 mm. pressure suffer a drop of 2° in temperature, the final volume will be $\frac{291}{293} \times 100 \times \frac{743}{745} = 99.05$ c.c. So that, under these conditions, a gas having no CO_2 would, if analyzed for CO_2, show 0.95 per cent CO_2, unless the correction were made. The factor $\frac{291}{293}$ is simply the ratio of the absolute temperature and the factor $\frac{743}{745}$ is the ratio of the atmospheric pressure minus the drop in aqueous tension to the atmospheric pressure. The general formula is

$$V' = V \times \frac{T'}{T} \times \frac{P \pm a}{P}.$$

V is the original volume, V' is the volume sought, T is the original absolute temperature, T' is the new absolute temperature, P is the barometric pressure and a is the change in aqueous tension.

Apparatus Used for Gas Analysis.—The writer much prefers the Hempel type of gas analysis apparatus for all ordinary gases and has given up the use of the Orsat's apparatus and other special built-up equipment. The Hempel type is so flexible and can be applied to the analysis of any kind of gas so satisfactorily that it is used for all work in the private laboratories in this Department. It takes more experience to manipulate the Hempel type, but in the hands of an experienced operator the results are very reliable.

The Orsat's type is widely used in connection with power plant chimney gas analysis and a description of it and its operation is given below in connection with the analysis of flue gas. Yet even here, the writer prefers the Hempel apparatus.

The Analysis of Flue Gas.—Orsat's apparatus is shown as connected for use in Fig. 22. The gas from the flue is drawn into the bottle *B* through the tube *A*. *B* contains absorbent cotton to filter out soot from the gas. From *B* the gas passes down into the bottle *D*, where it bubbles through about an inch of water and then goes through *F* to the aspirator. If the rate of aspiration is about 150 c.c. a minute, and the bottle *B* of 500 c.c. capacity, *D* will contain a sample of the gas representing the average of some minutes. *D* is connected with the analyzing apparatus as shown. In the apparatus, *P* is the gas measuring tube. *Q* is the water jacket. *S* shows the glass stop-cock that connects the gas tube

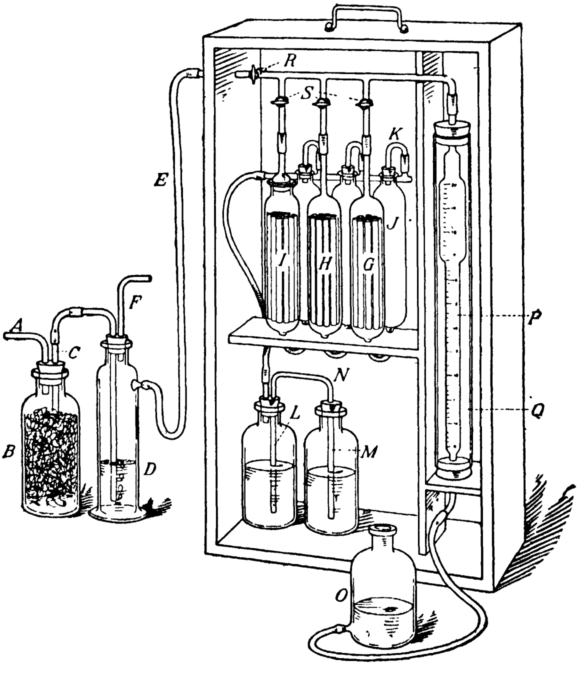

Fig. 22.

with the reagent tubes, *I*, *H* and *G*. These contain short lengths of glass tube to spread out the liquid and increase the active surface.

To fill the apparatus: Remove the old solution by first driving air over the gas tube into the absorbing bulbs. This is done by raising the pressure bottle and forcing the liquid all into the rear bulbs. Then empty each by a small siphon first filled with water and inserted to the bottom of the bulb. Now fill the first rear bulb *J* with the KOH solution. This serves to absorb CO_2 and also SO_2 and H_2S. It acts rapidly and completely and one filling will serve for from fifty to sixty gas analyses before its action begins to be too slow.

Put a good-sized funnel into the second rear bulb and weigh into it 30 grams of pyrogallic acid. Wash this down into the bulb with 200 c.c. of KOH solution (sp. gr. 1.55). If the apparatus will not hold the volume of solution, take less and reduce the pyrogallic acid proportionately; if it requires more, add more.

The third bulb is filled with the cuprous chloride solution. The glass tubes in this bulb contain spirals of copper wire, which keep the solution reduced.

Process of Analysis.—Fill all the reagent bulbs to the mark on the capillary tubes by opening the proper stop-cocks and lowering the pressure bottle carefully till the liquid rises to the right point. Do this with one bulb at a time, and on no account try to set the level of the liquid by opening or closing the stop-cocks. Bring it to the right point by raising or lowering the pressure bottle, and then close the stop-cock. Proceeding in this way, the fluid will never be drawn up into the stop-cock. Should such an accident happen, the stop-cock must be immediately taken out, washed and then relubricated with vaseline. The alkaline liquid, if allowed to remain in the glass stop-cock, would soon cause it to stick hopelessly. Now set the three-way cock so that the opening to the side is connected with the measuring tube. Raise the pressure bottle till the liquid fills the tube to the mark on the capillary. Turn the cock so as to close this connection and open the one to the sample inlet tube, lower the bottle and draw in slowly 50 or 60 c.c. of gas. This should be enough to completely wash out air in the connecting tubes. Again reverse the stop-cock, lift the bottle and run this gas, which is contaminated with that left in the connections and capillaries, out through the side tube. Now again reverse the stop-cock and draw in the sample of gas for analysis, lowering the bottle until the gas fills the measuring tube to some distance below the zero mark. Close the cock and set the pressure bottle on a support a little above the level of the zero point. Pinch the rubber near the bottom of the burette, open the cock to the side and carefully let the liquid run in by releasing the pressure of the fingers until it reads exactly zero on the tube. Now close the cock carefully, take down the bottle and read the volume of the gas after equalizing the pressure by bringing the surface of the liquid in the bottle to the level of that in the tube. The reading should be exactly zero. If it is 0.1 or 0.2 c.c. off, this can be corrected by raising or lowering the level of the water in the pressure bottle until the reading is zero, and making all subsequent readings in the analysis after giving the leveling bottle the same relative elevation.

The measuring tube now contains 100 c.c. of gas. Open the stop-cock into the potash bulbs and run the gas over by raising the pressure bottle. Be careful to hold the bottle so that the liquid will rise only to the mark in the gas tube. Now draw the gas back in the same way, run it over again and again back. Bring the potash solution carefully to the mark in its tube, close the stop-cock, wait at least 30 seconds for the liquid to drain down the side, level as before and read the volume. Transfer a second time to the potash, draw it back and read the volume again. If it does not agree with the first reading, run it over a third time. With fresh potash solution, the second reading should always check the first. The decrease in volume is the CO_2. Now proceed in the same way with the other tubes, using the pyrogallic solution first and then the cuprous chloride. With the pyrogallate tube, the gas should be run over two or three times rapidly before taking a reading, so that the dark saturated solution forming on the walls of the bulb may not remain long in contact with the gas, as this might lead to the formation of CO. The liquid draining down the side of the bulb will show by its change of color when it is absorbing oxygen. As soon as the oxygen is all absorbed, the liquid on the sides of the bulb will not turn brown as the gas reaches it. Always get two readings that agree before proceeding to the next tube. The corresponding decreases in volume give the oxygen and the CO. The residual gas is estimated as N_2. It will contain any H_2 and CH_4 present in the original gas, but these are rarely present in chimney gases in measurable amounts. When the analysis is finished, run out the residual nitrogen, leaving the measuring tube full of water. Now everything is ready for the next test.

Extreme care should be taken to avoid getting any of the absorption solutions into the connection or measuring tubes. Should this happen, they must be washed out and the water in the pressure bottle changed before starting a new analysis, as gas might be absorbed in filling the apparatus. The Orsat's apparatus may be used for the determination of CO_2 and CO in the gas from the iron blast furnace. In this case the residual gas invariably contains hydrogen and methane and should be kept for further analysis.

If the pipettes are of the "bubbling" type, the absorption is more rapid.

BLAST FURNACE AND PRODUCER GAS

These two gases are analyzed in the same way. The writer prefers the Hempel apparatus for the analysis of these gases rather than special built-up apparatus, because the Hempel is more convenient and is accurate. It is the writer's experience that results with the Hempel apparatus can, with care, be made accurate to 0.05 per cent. When greater accuracy than this is desired, it is necessary to use some form of apparatus such as the one evolved by Mr. Burrell of the Bureau of Mines and shown on page 348, or such as the Haldane apparatus. The complete analysis of a producer gas can be made in less than a half hour. What was said concerning sampling and storage of gas at the beginning of this chapter applies here. If the sample is taken over water, as when a long-time sample is taken, the surface of the water must be covered with paraffin shavings.

Before making a regular analysis, all the solutions should be saturated with the kind of gas which is to be analyzed by running through a preliminary analysis. This is important for accurate results.

It is essential that the room or laboratory in which the gas analysis is being carried out should be fairly constant in temperature and not subject to heavy draft of warm or cool air. If such a room with reasonably constant temperature conditions is not available, a stream of water from a main in which the temperature does not vary much or from an overhead barrel should be kept passing through the water jacket of the burrette. It is necessary even under the best of conditions to keep a record of the temperatures at the beginning and end of each determination and to make proper corrections

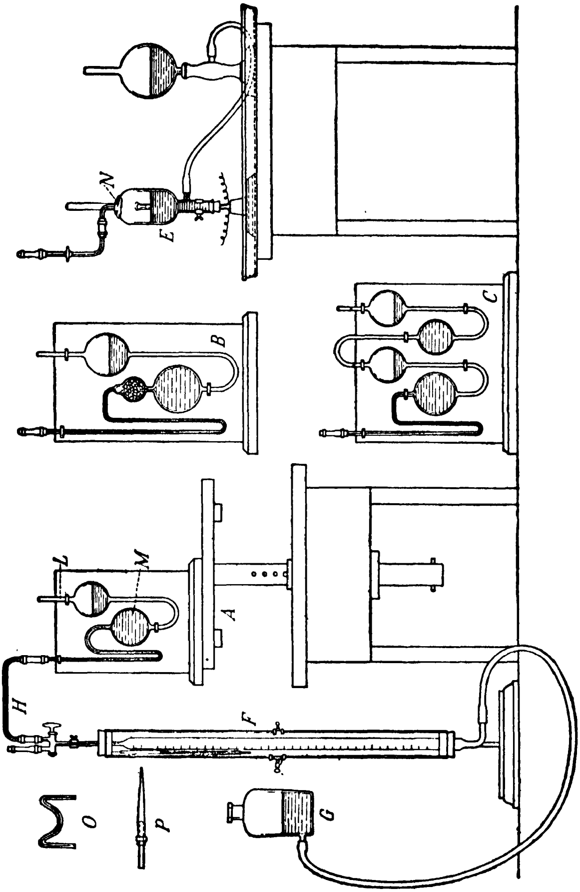

FIG. 23.

Apparatus Used.—*A* (Fig. 23) is a single pipette containing 30 per cent solution of KOH used for absorbing CO_2. *B* is a pipette filled with fuming sulfuric acid. The small upper bulb is filled with glass beads in order to give a larger surface of contact between the gas and the acid. This is used for absorbing the "illuminants" or unsaturated hydrocarbons, such as ethylene, C_2H_4, propylene, C_3H_6, etc. *C* is a double pipette containing alkaline pyrogallate for oxygen. The double pipettes containing ammoniacal cuprous chloride, are precisely the same as *C*. It is not necessary to use both on gases containing but traces of CO, but if the gases are blast-furnace gas, or producer gas, or coke-oven gas, or water gas it is necessary to use two cuprous chloride pipettes and even three are sometimes used. The combustion pipette containing a platinum spiral which can be heated with an electric current is shown in Fig. 24. It is made from a bottle with the bottom cut off, and inverted in mercury. A capillary tube with a stop-cock is attached, passing through a one-holed stopper through which two nichrome wires pass, projecting about ¼ in. and on the end of which the spiral is attached. The combustion pipette sets in a basin to catch the mercury should the tube break. *F*, Fig. 23, is the burette connected with a level-bottle ing *G*. The burette must be water jacketed and a thermometer should hang in the water of the jacket. It is convenient to have the stop-cock a three-way one, but not necessary. *H* is a capillary tube with an internal diameter between 0.5 and 1.0 mm., or about ¹⁄₄₀ in.

The rubber tubes on the pipettes should be made of thick-walled pure gum and should be wired to the pipettes by passing the wire around twice or more to prevent leakage. The rubber tube should project beyond the end of the capillary of the pipette about 1⅛ in. but not so long but that the air in the tube can be driven out by squeezing it between the thumb and forefinger. Also, and this is important, the tube should have a band of elastic rubber about it as shown in the cuts, in order to make a tight connection when the capillary on the burette is pushed in the tube. This band is put on as follows: Cut a piece of pure gum tubing a little smaller in diameter than the rubber tube on the pipette and about a quarter of an inch long. Push this on a tapering glass tube (*P*, Fig. 23) until it is at the big end, which should be as large in internal diameter as the rubber tube on the pipette. Push the rubber tube into the glass tube about ¼ in. and then push the rubber band off the glass tube onto the rubber tube. This will make the burette capillary fit in the rubber tube without leaking gas and without the bother of tying the connection each time.

Filling the Pipettes.—To fill the single pipettes, simply pour the reagent in the large tube *L* until there is enough to fill the bulb *M* and to have about ½ in. of the reagent in the other bulb.

To fill the double pipettes, first pass an oxygen- and carbon-monoxide-free gas, such as natural gas or hydrogen, through the pipettes until the air is displaced. Then attach to the capillary of the pipette a rubber tube the end of which dips into the reagent which is to be put in the pipette, then suck on the other end of the piette until enough of the reagent has entered to fill the first bulb full and about ½ in. in the second. A little experience makes this easy. Then pour into the rear bulb 125 c.c. of water to act as a water seal to keep out the air. The purpose of filling the bulbs with a neutral gas is to prevent the weakening of the reagent by air in the bulbs.

The reagents are prepared as directed on page 319 *et seq.*

Process of Analysis.—First see that the water in the burette jacket is at the same temperature as that in the leveling bottle. The water in the leveling bottle should be shaken with some gas similar to that to be analyzed and so should the absorption solutions in the pipettes, in order to saturate the liquids with the gas other than the constituent to be absorbed in the solution. This is most readily done by making a preliminary analysis of the gas. Then see that the burette is tight by taking a reading, then raising or lowering the pressure bottle and allowing the gas to stand under a pressure or vacuum for several minutes. Then take another reading. The readings ought to agree exactly. In reading the burette, hold a finger or piece of paper back of the burette and a little below the meniscus so as to illuminate the bottom of the meniscus and make the reading sharp. With care, one can be sure of the reading to within less than 0.05 c.c. The water in the pressure bottle should contain about 0.5 per cent H_2SO_4.

Now raise the pressure bottle until all gas is out of the burette and water drops from the end of the capillary. Also, wash the capillary by dipping the end of it in acidulated water to remove all alkali. Then attach the rubber tube of the vessel containing the sample to the burette capillary, first taking care to drive all air out of the rubber tube. Then lower the pressure bottle of the burette and raise the pressure bottle of the vessel containing the sample and open the stop-cock on the burette and draw in the gas until a little more than 100 c.c. has been drawn in. Close the stop-cock and detach the sample vessel. Allow the burette to drain about 30 seconds. Raise the pressure bottle until the bottom of the meniscus is just on the zero (or 100-c.c.) mark, pinch the rubber tube connecting the burette and bottle and open the stop-cock momentarily to put the gas under atmospheric pressure. Close the cock and level the water in the burette exactly with the water in the bottle and take the reading. It should read exactly zero (or 100 c.c.). At the same time read the temperature of the jacket water.

Now attach the KOH pipette to the capillary of the burette as follows: Squeeze the rubber tube on the pipette between the thumb and forefinger so that all air will be driven out of the tube and the KOH will fill the capillary of the pipette. Drop with a finger a drop of water on the end of the rubber tube, then push the capillary of the burette into the rubber tube in such a way as not to drive air into the tube and until the ends of the capillaries are in contact. The KOH should extend to the top of the pipette capillary. Make a mental note of its position. Now open the stop-cock and raise the pressure bottle and drive all the gas over into the pipette. Close the cock and shake the KOH pipette vigorously for 20 or 30 seconds, then raise the pressure bottle and run a few drops of water into the pipette to wash all KOH which was splashed into it out of the capillary. Then lower the pressure bottle and draw the gas back into the burette until the KOH rises in the capillary of the pipette exactly to the same height as it was at the beginning. Allow the burette to drain as long as before and take the reading of the burette carefully, also read the temperature of the jacket. The decrease in volume (if there has been no temperature change) is the percentage of CO_2 in the gas. To make sure that the CO_2 is all absorbed, repeat the above operation. The reading should be the same as before. If not, run a blank determination by again repeating the operation of driving the gas into the KOH pipette, etc., and again read the burette after the usual draining. If there is a further change of volume, either positive or negative, it shows that there is a leak or that the temperature is changing. Twice this change in volume should be added to or subtracted from the second reading. By taking this trouble of running a blank, the results can be relied upon to 0.05 per cent. For most technical work, such care is not necessary but should be taken occasionally to check up the work. If there is a leak, of course, the apparatus must be corrected.

Now remove the KOH pipette and attach the fuming sulfuric acid pipette in the same way, making mental note of the position of the acid in the capillary. The connection must be especially tight, as it requires considerable pressure to drive the gas into this pipette. Raise the pressure bottle and drive the gas into the burette, *but do not let any water get into the sulfuric acid pipette.* Pass the gas back and forth between the burette and pipette three times, then bring the sulfuric acid back to the original place on the capillary. The gas now has sulfuric acid vapors in it which must be removed by passing the gas into the KOH pipette and shaking vigorously. Finally, bring the gas back into the burette and read the change in volume and temperature. If there has been no temperature change, the decrease in volume is the percentage of "illuminants," chiefly C_2H_4. The C_2H_4 is changed into $C_2H_6S_2O_7$. Any acetylene is changed to $C_2H_4SO_4$ and benzene to $C_6H_6SO_3$. Since blast-furnace gas contains no heavy hydrocarbons, the fuming sulfuric acid is not used when blast-furnace gas is analyzed.

It is well to run a blank on this determination occasionally.

Next, attach the pyrogallate pipette and manipulate just as with the KOH pipette, except that the shaking of the gas in contact with the solution should be much longer. The decrease in volume is the percentage of oxygen. To make certain of complete absorption of the oxygen, it is necessary to run the gas into the pipette again. There should be no change in volume.

If there is more than a trace of oxygen in the gas it will be apparent by the production of a red color in the film of pyrogallate on the walls of the bulb. As soon as the oxygen has all been absorbed and the bulb is shaken further, there will be no more production of this red color.

The pyrogallate pipette should be shaken while the gas is running into the pipette if the gas contains much oxygen, to avoid any danger of the formation of carbon monoxide by complete oxidation of the thin film of the pyrogallate on the walls of the bulb. Of course, blast-furnace gas contains no oxygen except accidentally.

Next attach the ammoniacal cuprous chloride pipette and manipulate as with the pyrogallate pipette. The CO is absorbed slowly and the pipette should be shaken at least 100 times, and if the cuprous chloride has been used before, the gas must be run into a second cuprous chloride pipette and shaken 100 times. This is always the best way if the gas contains more than 2 per cent of CO. When the first pipette gets too slow in its action, it is emptied and filled with fresh solution and used as the second pipette, while the other one is used first.

The gas now has left in it only hydrogen, methane and nitrogen.

The hydrogen and methane may be determined by explosion, slow combustion with a hot platinum spiral or by slow oxidation in contact with hot copper oxide. The writer does not like the first method and has ceased using it. The other two methods are both quite satisfactory with preference, perhaps, for the copper oxide method. The slow combustion method, using a hot platinum spiral, will be described here and the copper oxide method will be described under the analysis of coke-oven gas. The only drawback to the platinum spiral method is the danger of the spiral becoming too hot during the determination and melting, thus losing the determination. Aside from this the method is excellent.

Slow Combustion with a Platinum Spiral.—Attach the combustion pipette to the capillary of a burette containing oxygen and run in enough oxygen to uncover the platinum wire and its connections, but do not use more than 40 c.c. Measure the oxygen carefully and the temperature of the burette from which it was taken. Close the stop-cock of the pipette and attach it to the capillary of the burette containing the gas. Connect the wires from a source of electricity to the terminals of the wires of the combustion pipette. Turn on the current until the platinum wire in the pipette is at a dull yellow of nearly the same brightness as an ordinary incandescent-light carbon filament. Record the temperature of the gas, then open the stop-cocks on the burette and the pipette and run the gas into the pipette slowly, in order, in the case of producer gas, to prevent an explosion or melting of the platinum. The mercury in the leveling bulb of the pipette should be at about the same level as the mercury in the pipette in order to avoid leaks due to the great pressure caused by considerable difference in levels of the mercury. After the gas is all in the pipette, close the pipette stop-cock and continue the combustion for several minutes. The pipette should be kept cool during the combustion by being completely immersed under water. Now shut off the electric current and run the residual gas back into the burette. Allow the gas to cool a minute and then read the volume and temperature. If there has been any change in temperature, make the proper correction. Call the contraction in volume *C*. Now attach the burette to the KOH pipette and determine the CO_2 produced by the burning of the CH_4. The methane in the gas was the same in volume as the CO_2 produced by its combustion, and, since the original sample was 100 c.c., the volume of CO_2 produced in cubic centimeters is the percentage of methane in the gas sample. The contraction in volume due to the burning of the methane is twice the volume of the methane, and this contraction subtracted from the total contraction *C* on burning gives the contraction due to the burning of the hydrogen, which multiplied by two-thirds gives the volume and percentage of the hydrogen.

The reactions are: CH_4 (1 vol.) $+ 2O_2$ (2 vol.) $= CO_2$(1 vol.) $+ 2H_2O$. Since the H_2O condenses, the contraction is twice the CH_4.

$2H_2$(2 vol.) $+ O_2 = 2H_2O$. Since the H_2O condenses, the hydrogen is equal to two-thirds of the contraction when it is burned.

The total time required for the analysis of the gas is about 25 minutes.

Notes on the Process.—The two cuprous chloride pipettes may be permanently connected by means of a T-capillary, with a stop-cock in each branch going to a pipette, and the third branch connected to the burette. In this way only one operation of connecting the cuprous chloride pipettes to the burette is necessary, although each pipette works separately.

If the stop-cock on the burette is a "two-way" one, it is convenient to attach the KOH pipette permanently to one of the ways because the KOH pipette is used three times during the analysis, and a permanent attachment of it saves the time of three operations. This idea has been carried out to the extent of having a stop-cock with enough different "ways" to have a permanent attachment for each pipette.

After each time that a pipette is connected to the burette a drop of water should be placed on the top of the rubber connection, so that if the connection is leaking, the bubbling of gas through the drop may be seen.

The combustion pipette should hold about 150 c.c. The platinum wire should be inserted far enough in so that 40 c.c. of gas in the pipette will uncover the wire and prevent the mercury from short-circuiting the current. The pipette must be surrounded with a wire netting or gauze so that the eyes of the operator will be protected if an explosion should take place. It is convenient to have a stop-cock on the combustion pipette, but is not necessary. If a stop-cock is not used, it is necessary to close the rubber tube on the capillary with a glass plug when the pipette is moved from the oxygen burette to the burette containing the gas.

A very satisfactory combustion pipette may be easily made as shown in *A*, Fig. 24. It consists of a 250-c.c. bottle with the bottom cut off and with the mouth of proper size for a No. 3 rubber stopper. Through this rubber stopper pass two nichrome wires with a platinum spiral arranged as above described. A porcelain or asbestos disk is attached to the bottom of the stopper to prevent the rubber becoming hot and giving off vapors. The bottle, which is the combustion pipette, is immersed open end downward in a jar of mercury with a sufficient amount of mercury to come up to the level of the stopper when the bottle is resting on the bottom. Through the single hole in the rubber stopper passes a capillary tube with a stop-cock which is connected to the capillary of the measuring burette in the usual fashion. Owing to the rubber connection of the burette capillary, the combustion pipette rises and sinks in the mercury as gas passes in and out, thus automatically adjusting itself without danger of pressure sufficient to cause leaks. The jar containing mercury is kept filled with water so that the combustion pipette is always submerged and cooled. The tube *B* is a capillary tube in this method but is a CuO tube in the CuO method.

The platinum wire must be heated to a dull yellow or the combustion is likely to be incomplete. The wire may be heated by about three or four dry cells or, better, by the current through six 16-cp. electric lights placed in parallel on a 110-volt circuit. That is, a current of about 3 amp. is required, depending, of course, on the diameter of the wire. If the wire is heated hotter than a dull yellow, a slight error is caused, due to formation of N_2O_4.

When a gas contains ethane as well as methane and hydrogen, which is not the case with producer or blast-furnace gas, the hydrogen must be determined separately, as directed under the analysis of coke-oven gas.

Of course the hydrogen in producer or blast-furnace gas may be determined separately, but this is not necessary. If the gas contains hydrogen and no methane, the combustion pipette may be filled with water instead of mercury. Blast-furnace gas contains only about 0.2 per cent methane. If the gas contains both hydrogen and methane and the hydrogen is removed first, the combustion of methane may be made without mercury.

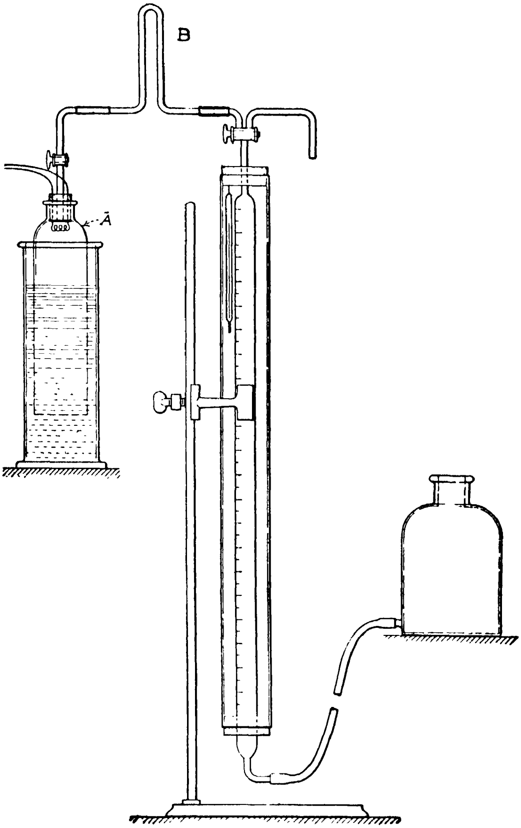

FIG. 24.

Gas Analysis without Use of Cuprous Chloride.—Instead of absorbing the CO in cuprous chloride and then determining the hydrogen and methane by combustion, the carbon monoxide, hydrogen and methane may be all determined together by combustion without having to use the cuprous chloride. This applies only to gases like producer and blast-furnace gases which have no hydrocarbons higher than methane.

Process of Analysis.—Carry out the combustion exactly as above directed. Measure the decrease in volume after combustion, and then determine the CO_2 produced by the combustion by passing the residue into the KOH pipette. Then determine the amount of oxygen left after the combustion by absorbing it in pyro solution. Also carefully determine the amount of oxygen in the volume of oxygen used by passing the same volume of oxygen through the pyrogallate pipette. The difference between the two gives the amount of oxygen used. Calculate the results as follows: The reactions of combustion are as given above for hydrogen and methane and as follows for carbon monoxide: $2CO$ (2 vol.) $+ O_2$(1 vol.) $= 2CO_2$(2 vol.). Let $x =$ hydrogen, $y =$ methane and $z =$ carbon monoxide. Then we have the following equations:

Contraction during combustion $= \frac{3}{2}x + 2y + \frac{1}{2}z.$
Carbon dioxide produced $= y + z.$
Oxygen consumed $= \frac{1}{2}x + 2y + \frac{1}{2}z.$

Combining these equations we get the relations:

Hydrogen = contraction minus oxygen consumed.

Methane = oxygen consumed minus $\frac{1}{3}$ contraction minus $\frac{1}{3}$ CO_2 produced.

Carbon monoxide $= \frac{4}{3}$ CO_2 produced plus $\frac{1}{3}$ contraction minus oxygen consumed.

Notes on the Process.—This method requires less time for manipulation but more time for calculation than the one previously given. They are about equally accurate.

There is a correction necessary for accurate work when a gas is burned which gives a large amount of CO_2. It is due to the fact that the molecular volume of CO_2 is 22.26 liters, while that of CH_4 is 22.44 liters and of CO is 22.39 liters. That is, the CO_2 produced by burning 100 c.c. of methane is 99.20 c.c. instead of 100 c.c., because CO_2 departs considerably from being a perfect gas. Hence, when CO or CH_4 are burned, the contraction in volume should be corrected by subtracting from it 0.8 per cent of the volume of CO_2 produced and the volume of the CO_2 should be increased by 0.8 per cent of the measured amount of CO_2 in order to calculate the volume of the methane or the CO.

The determination of dust in unwashed blast-furnace gas is an exceedingly difficult proposition. For the apparatus and details used for this determination, see TOUZALIN and BRADY, *J. Ind. Eng. Chem.*, III, pp. 662–670.

The Analysis of Coke-oven Gas and Retort Gas.—Up to the combustion, the analysis of this gas is carried on in exactly the same manner as for producer gas, except for the following: Since coke-oven gas and retort gas have a rather large amount of "heavy hydrocarbons," the absorption of them in the fuming sulfuric acid should be given more time. After determining the "heavy hydrocarbons," run the gas over into the sulfuric acid to see if a further contraction is obtained. If it is, more time for the absorption must be used.

Since coke-oven gas and retort gas contain hydrogen, methane and ethane, the hydrogen must be separately determined, because the combustion data are sufficient only for the determination of one hydro-carbon in the presence of hydrogen.

The separation of hydrogen from the methane and ethane is a process of selective oxidation, the conditions of oxidation being such that hydrogen is oxidized with only very little oxidation of the hydrocarbon. Two methods are used: the palladiumized asbestos method and the copper oxide method. Both methods are satisfactory.

Determination of Hydrogen by Combustion in Contact with Palladium.—When a gas containing hydrogen in the presence of methane and ethane is mixed with oxygen and passed over palladium heated to 90 to 100° C., the hydrogen is completely burned to water but the methane and ethane are unaffected if the temperature is not allowed to rise too high. If the gas contains much hydrogen, it should not be passed over the palladium so fast as to cause the palladiumized asbestos to glow, for then some methane will be oxidized.

The palladiumized asbestos is prepared as follows: Dissolve 1 gram of palladium in aqua regia, evaporate the solution to dryness on a water-bath, so as to remove any adhering hydrogen chloride as completely as possible, and dissolve the palladium chloride thus produced in a very little water. To this add a few cubic centimeters of a cold saturated solution of sodium formate and sufficient sodium carbonate to produce a strongly alkaline reaction. Now introduce 1 gram of very soft, long-fibered asbestos, which, if any excess of water has been avoided, absorbs the whole liquid and forms with it a thick paste. This is dried at a gentle heat, by which process black, finely divided palladium is uniformly precipitated upon the asbestos fiber. In order to make the palladium adhere, the asbestos thus prepared must be heated on a water-bath till completely dry, then soaked in a little warm water, put into a glass funnel and freed from all adhering salts by thorough washing, without removing any palladium. After drying, the substance exhibits a dark gray color, has a slight tendency to stain the fingers and contains 50 per cent palladium. It possesses a very high degree of chemical activity; in the perfectly dry state it can cause the combination of hydrogen and oxygen, even at the ordinary temperature, but, in order to secure this result, it is always employed in the heated state.

For the preparation of the capillary combustion tubes, employ capillary glass tubing of about 1 mm. bore and 6 mm. outside diameter, cut in pieces 16 or 18 cm. long and bent as shown at *O*, Fig. 23. The asbestos fiber must be introduced into them before bending off the end, in the following way: a few loose fibers of the palladium asbestos are laid alongside each other on smooth filter paper up to a length of 4 cm.; they are moistened with a few drops of water, and, by sliding the finger over them, are twisted into a fine straight thread, which in the moist state has the thickness of stout sewing cotton. This thread is grasped at one end with the nippers, and, without bending or nicking, is slid from above into the capillary tube, which is held vertically. This is then filled with water by means of the washing bottle, and, by jerking or by drawing off the water, the asbestos thread is brought into the center of the tube. This is now allowed to dry in a warm place. It is well to have small bulbs blown near each end of the tube to prevent films of water getting to the palladium.

Procedure for the Determination of Hydrogen.—After the CO has been determined by absorption in cuprous chloride, transfer one-half of the remaining gas back into the cuprous chloride pipette, keeping the other half in the burette. This may contain as high as 30 c.c. of hydrogen. Draw into the burette 15 c.c.

of oxygen and then enough air to fill the burette to 100 c.c. There will now be about twice as much oxygen present as is theoretically necessary to burn the hydrogen. Carefully read the burette and its temperature. Then attach the palladiumized asbestos capillary, place a small beaker of water under it so that the capillary is immersed, heat the water to boiling and attach the other end of the capillary to a Hempel pipette containing only acid water. Pass the gas through the palladium capillary at the rate of about 15 c.c. per minute, taking care that the gas does not pass through so rapidly that the heat generated by the burning hydrogen causes the palladium to glow. Do not allow the water of the burette or pipette to rise up to the palladium. When the gas has all passed over, draw it back into the pipette and carefully read the volume and temperature. The hydrogen should be all burned, but, to make sure, again pass the gas over and back. There should be no change in volume the second time. The total contraction multiplied by $\frac{2}{3}$ gives the hydrogen present and this multiplied by 2 gives the percentage of hydrogen.

Now, to see if any methane has been burned (none should have been if the palladium was not allowed to glow), pass the gas into the KOH pipette. If any CO_2 is found, some methane was burned and a correction must be made.

Determination of the Methane (and Ethane).—Measure about 75 c.c. of oxygen and pass it into the combustion pipette. Heat the platinum spiral to a bright yellow and carry out the combustion as directed under the analysis of producer gas, except that the combustion must be made more carefully and slowly because of the more inflammable nature of the gas. Accomplish this as follows: Place a screw-cock on the rubber tube connecting the pressure bottle with the burette level to bring the gas to atmospheric pressure, level, screw the screw-cock shut and place the pressure bottle on a shelf a couple of feet above the top of the burette. Open the stop-cocks between the burette and combustion pipette (Fig. 24), then loosen the screw-cock so that the gas passes into the combustion pipette at the rate of 10 c.c. per minute. When the gas is all in the combustion pipette, continue the glowing of the spiral for several minutes to assure complete combustion. After the combustion, determine the contraction in volume and the CO_2 produced.

From the contraction in volume obtained, subtract the contraction due to the burning of the hydrogen. This gives the contraction due to the burning of the methane and ethane. Then let x = the CH_4 and y = the C_2H_6. We have the relations:

$$\text{Contraction} = 2x + 2.5y$$

and

$$CO_2 = x + 2y.$$

Solving, we get

$$x \text{ (or methane)} = \frac{4 \times \text{contraction} - 5CO_2}{3}, \text{ or } CH_4 = CO_2 - 2C_2H_6$$

and

$$y \text{ (or ethane)} = \frac{(4CO_2 - 2 \times \text{contraction})}{3}.$$

The reaction for the combustion of ethane is:
$2C_2H_6$ (2 vol.) + $7O_2$(7 vol.) = $4CO_2$(4 vol.) + $6H_2O$ (condensed).

The results obtained for methane and ethane, when multiplied by 2, give the percentage in which they were present in the sample. The oxygen consumed may be determined to check the results.

Notes on the Analysis of Coke-oven Gas.—The gas is apt to contain some hydrocarbon vapors, such as C_6H_6, etc. For their determination see page 372.

The fuming sulfuric acid absorbs the olefins (C_nH_{2n}), acetylene (C_2H_2), the benzene hydrocarbons, such as C_6H_6, and the higher paraffin hydrocarbons, such as C_5H_{12} and C_6H_{14}. If it is desired to know how much benzene is present, the total heavy hydrocarbons are determined by absorption in fuming sulfuric acid. Then in another sample they are absorbed with a standard bromine solution. The bromine combines with the ethylene to form $C_2H_4Br_2$, but does not combine with the benzene. The excess bromine is titrated with potassium iodide and sodium thiosulfate, from which the ethylene can be calculated. (HABER and OECHELHAUSER, *Ber.* **29**, 2,700.) At coke-oven works the benzene with toluene and xylene is determined by passing the gas through absorbing bottles containing cooled paraffin oil (sp. gr. 0.89) boiling point 360°C. The gas dried by passing over $CaCl_2$ is passed through these bottles cooled by ice, the bottles connected by glass, not by rubber, until a large volume has passed through at about 2 c.c. per second. The increase in weight of the bottles gives the weight of benzene hydrocarbons absorbed.

Benzene is absorbed somewhat by water and KOH solution; therefore, if the gas contains benzene, either the fuming sulfuric acid must be used before the KOH or the KOH must be saturated with the same kind of gas. Alkaline pyrogallate absorbs a small amount of the higher paraffins (*Bull.* 42, U. S. Bureau of Mines).

Upon prolonged contact, fuming sulfuric acid will absorb some methane and ethane. This, however, is negligible if the time of contact is not prolonged beyond five or ten minutes. The same is true of bromine.

According to Fritzche (*Z. f. angew. Chem.* (1896), 456) ethylene can be separated from butylene by sulfuric acid (sp. gr. 1.62) which dissolves butylene but not ethylene.

Cuprous chloride absorbs ethylene and acetylene. These gases therefore must be removed before the CO. It also slightly dissolves the higher paraffins.

Copper Oxide Method of Combustion.—Copper oxide has long been used in coal analysis and organic analysis for the combustion of gases given off from these materials, but it has only been used in gas analysis comparatively recently. Its usefulness depends upon the fact that at certain temperatures one gas can be oxidized while other gases are only slightly affected. The following table by Campbell (*Am. Chem. J.*, **17,** 688) shows how the principle of selective oxidation can be used for gas analysis.

Gas	Pure CuO, Degrees Centigrade	Pd.—CuO, Degrees Centigrade
H_2	175–180	80–85
CO	100–105	100–105
C_2H_4	315–325	240–250
C_3H_6	270–280	220–230
C_4H_8 (Iso)	320–330	270–280
CH_4	Above 450	

The above temperatures are for initial combustion.

Copper Oxide Tube.—The details of the copper oxide tube are shown in Fig. 26. Thin walled pyrex tubing of 4 mm. inside diameter is bent into the form of a U. It is cut off according to the dimensions of Fig. 26 and filled with approximately 3.5 grams of fine "wire" oxide. The oxide is held in place by small plugs of glass wool in both ends of the tube. Capillary tubing of 1.5 mm. internal diameter is sealed onto the ends of the thin-walled U-tube containing the oxide, for making connection to the train. The entire free space of the U-tube from one stopcock to the other should not exceed 2.5 c.c. A straight silica tube is also fairly satisfactory.

The construction of the electric heater for raising the temperature of the copper oxide to 300°C. is shown in Fig. 25. The heating element is made of 50 ft. of No. 22 gage B. & S. nichrome wire wound in helical coil. This can be done conveniently by winding the wire on a spindle 3⁄16 in. in diameter, using a lathe. The helix is then coiled around a grooved alundum tube of 2 in. internal diameter. The distance between adjacent coils is sufficient for ample electrical insulation. Heat insulation is secured by covering the outside of the heating element with a 1 in. thick layer of a mixture of magnesium oxide, asbestos fiber and sodium silicate. The outer covering may be two layers of asbestos paper, or sheet metal. The ends are closed with circular pieces of transite board held together by three stay-bolts. The two ends of the wire coil are brought out to two binding posts mounted on the base of the heater. The furnace must be thoroughly dried for several hours at 100°C. before use. The winding described is for use with 110-volt current, which will raise the temperature to 300°C. in 15 minutes, using a current of 1.1 amp. The current is then reduced to about 0.7 amp. by use of a 50-ohm rheostat. A ther-

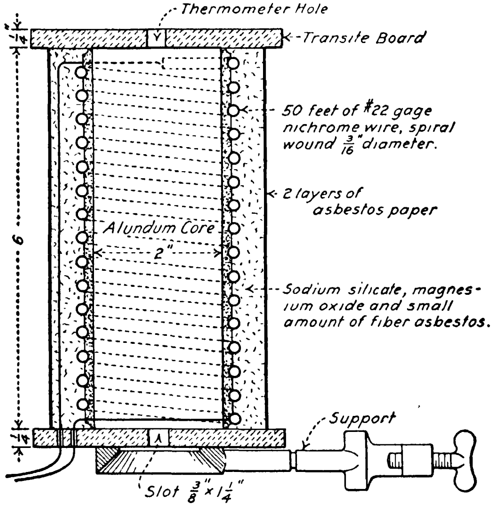

FIG. 25.

mometer for indicating temperature is inserted through a small hole in the top of the furnace.

Process of Analysis with Copper Oxide.—The gas has had removed from it, by the regular analytical procedure, all the CO_2, illuminants, oxygen and CO, and still contains the hydrogen, methane ethane and nitrogen.

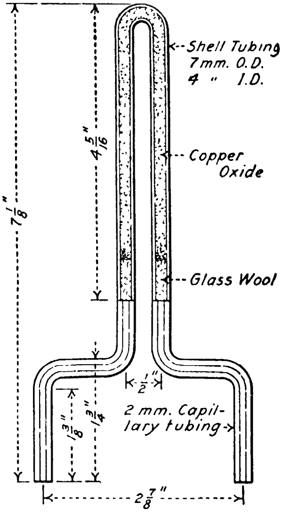

FIG. 26.

The apparatus used is shown in Fig. 24. It consists in a water-jacketed burette with a three-way cock, a floating pipette with a stop-cock and a copper oxide tube connecting the floating pipette and the burette. The other way of the stop-cock is connected to a KOH pipette. The floating pipette is made by cutting the bottom off of a 250 c.c. exactly the same as the combustion pipette described on page 335. It is very convenient to use for this purpose, because it adjusts itself to the volume of gas in it without noticeable change in pressure.

The chief error in the above combustion method comes from the absorption of the CO_2 in the burette water. This is obviated by the use of mercury. Also, any hydrocarbons higher than ethane introduce error, but these are present in small amounts.

Place the electric heater over the copper oxide tube and raise the temperature to a bright red. While this temperature is rising, store the residual gas left in the burette by passing it over into the NaOH pipette, draw air into the burette and, as soon as the copper oxide tube is red hot, pass the air back and forth through the copper oxide tube, connected as shown in Fig. 24, until only nitrogen remains (this is to oxidize the copper which has been reduced by the previous analysis of another gas sample). Store the nitrogen remaining in another pipette, then draw in more air and repeat the oxidation of the copper until no further oxygen is consumed. (Each analysis of coal gas consumes about 85 c.c. of oxygen.) Remove the heater and cool the combustion tube to atmospheric temperature. (If the combustion tube is of silica, it can be cooled immediately with water, but if of pyrex, a blast of air should be used.) While the tube is cooling, draw the nitrogen previously stored in the pipette back into the burette and connect the burette with the copper oxide tube. This leaves the tube filled with nitrogen, which is necessary. As soon as the tube is completely cooled, draw the mercury in the floating pipette into the capillary, close the stop-cock, pass the remaining nitrogen in the burette into the air and draw in the residual gas containing the hydrogen, methane, ethane and nitrogen, finally drawing in dilute H_2SO_4 to make sure that the capillary at the top of the burette is not alkaline. Carefully read the volume and temperature of the jacket water, open the connection to the copper oxide tube and raise the temperature by means of the electric heater to 250°C. Then pass the gas from the burette through the copper oxide tube into the floating pipette. Repeat the passage of the gas over the copper oxide until no further contraction can be noted. Usually passing the gas over and back twice, that is four times over the copper oxide, is sufficient for the oxidation of the hydrogen. Remove the heater, cool the combustion tube to atmospheric temperature, level and read the volume in the burette and the temperature of the jacket water. The contraction (when corrected for any temperature change) is equal to the volume of the hydrogen in the gas. The reaction is: $2CuO + H_2 = Cu_2O + H_2O$. A small amount of hydrocarbon may have been oxidized, but no attention need be paid to it at this point since the volume of CO_2 produced by burning methane is practically the same as the methane.

Replace the electric heater on the combustion tube, open the connection to the burette, raise the temperature of the copper oxide to a bright red and pass the residual gas slowly over the copper oxide as directed above for the operation of the combustion pipette. When the gas is all passed over, bring it quickly back, shut off the stop-cock connecting with the combustion tube, carefully read the volume and pass the gas into the KOH pipette. After absorption of the CO_2, bring the gas back into the burette and again read. Again pass the gas slowly over the copper oxide and determine the amount of CO_2 produced as before. Repeat this operation until no more CO_2 is produced.

If the temperature of the copper oxide is sufficiently high, the combustion ought to be complete the second time. Add the CO_2 produced by the various oxidations together, calculate its volume back to the temperature of the original sample and make corrections as indicated in the table on page 321. The purpose of absorbing the CO_2 after each passage over the copper oxide is to avoid absorption of the CO_2 in the water in the burette. If mercury is used in the burette, this is not necessary.

Remove the electric heater and cool the copper oxide tube to room temperature with the cock connecting with the burette open, draw the mercury in the floating pipette up to the original mark, close its stop-cock, level and read the volume in the burette and the temperature of the jacket water. The volume corrected to the original temperature is the amount of nitrogen in the original sample.

The volume of the nitrogen subtracted from the volume left after the removal of the hydrogen is the volume of the methane and ethane. Call this volume "hydrocarbons," and calculate these by use of the following equations:

$$CH_4 + 2C_2H_6 = CO_2 \text{ and } CH_4 + C_2H_6 = \text{Hydrocarbons.}$$

Notes.—It is especially necessary in a long analysis like this that the temperature should remain constant, otherwise tedious corrections have to be made. This constant temperature is most easily obtained by circulating, through the water jacket of the burette, water from a main of constant temperature or from an overhead tank.

It is possible to determine the hydrogen and carbon monoxide together by selective oxidation, determining the CO by the CO_2 produced and then the methane and ethane as above directed. The difficulty with this is that the higher hydrocarbons oxidize at a low temperature to a certain extent and produce CO_2, making the result for the ethane and carbon monoxide inaccurate.

Oxygen may be used instead of air for the reoxidation of copper oxide, but since it is necessary to have the nitrogen to fill the combustion tube before the analysis starts, it is convenient to use air to oxidize the copper oxide, thus leaving nitrogen ready for use. It is best after each analysis to reoxidize the copper oxide.

A silica tube for the copper oxide tube is much better than any glass tube, since it has no tendency to break on account of quick cooling, even by quenching with water. A straight silica tube may be satisfactorily heated by a fish-tail top burner protected from draft by an asbestos hood.

It is sometimes doubtful if the hydrocarbons are completely oxidized. In this case draw into the pipette about 50 c.c. of air and pass the mixture back and forth through the hot combustion tube and determine any CO_2 produced.

References:

White, "Gas and Fuel Analysis."
"The Gas Chemists Handbook," 2nd ed.

Analysis of Natural Gas

According to the experience of Mr. Burrell of the Bureau of Mines, the natural gas of this country does not contain any unsaturated hydrocarbons, although a slight absorption is obtained with fuming sulfuric acid, due to the absorption of other hydrocarbons. Neither does the gas contain carbon monoxide or hydrogen. These gases should never be reported as present in natural gas unless a qualitative test is obtained for them. The test for unsaturated hydrocarbons is made as follows: Prepare a 1 per cent neutral solution of palladous chloride ($PdCl_2$) containing 5 per cent sodium acetate and pass a large volume of the gas through the solution after first passing it through a KOH solution to remove any H_2S present. If there is any ethylene in the gas, it will reduce the palladium and a black precipitate of palladium will settle out. Any CO will also reduce the palladium but, as it is oxidized to CO_2, its presence may be detected by passing the gas through $Ba(OH)_2$ after passing through the palladous chloride. (See Brunck, *Z. angew, Chem.*, **25**, 2479.) For the blood test, I_2O_5 test and tannic acid test for CO, see page 352.

Process of Analysis.—Draw into the burette 100 c.c. of the gas and absorb the CO_2 in KOH and the oxygen (some may have leaked into the sample) in the pyro solution. Then run the gas back into the pipette. Carefully measure about 100 c.c. of oxygen, take its temperature and pass it into the combustion pipette. Then carefully draw just one-third of the gas from the pyrogallate pipette into the burette. Pass an electric current through the platinum spiral to heat it to a yellow heat while the top is kept cool by being immersed in water, and then pass the gas into the pipette carefully so that not more than 10 c.c. passes per minute. This is best done by entirely closing the tube connecting the leveling bottle with the burette with a screw-cock, then setting the leveling bottle up high, then carefully opening the screw-cock until the gas is slowly passing into the combustion pipette.

After the gas has all passed over into the pipette, keep the platinum spiral hot for several minutes to insure complete combustion. Then break the circuit, allow the gas to cool a minute or so and run the gas back into the burette. After proper drainage, read the volume of the gas and its temperature. Then pass the gas into the KOH pipette and determine the amount of CO_2 produced by the combustion. The methane and ethane are calculated as directed on page 345. Trifling amounts of oxides of nitrogen may be produced by the combustion.

In order to check the result, another third of the gas may be taken from the pyrogallate pipette and the combustion repeated. It is necessary to remember that the capillary of the burette holds an appreciable volume and in taking a fraction of a sample in this way this volume must be taken into account. The volume of the capillary may be determined by drawing into the burette some air or gas, reading the volume, then dipping the end of the capillary under water and drawing water into the capillary until it is filled and reading the volume again. The difference is the volume of the capillary.

The combustion pipette should be surrounded with a wire screen to protect the operator in case of an explosion.

It has been assumed that the only hydrocarbons present are methane and ethane. There may be higher hydrocarbons present. These are determined by absorbing them in absolute alcohol. Their solubilities in alcohol are as follows:

1 volume of alcohol dissolves	0.52 volumes of	CH_4	at 0°C.
1 volume of alcohol dissolves	1.50 volumes of	C_2H_6	at 0°C.
1 volume of alcohol dissolves	6.00 volumes of	C_3H_8	at 0°C.
1 volume of alcohol dissolves	18.00 volumes of	C_4H_{10}	at 0°C.

Pass into the combustion pipette, or another one filled with mercury, 2 c.c. of absolute alcohol or 1 c.c. of kerosene, then pass in about 100 c.c. of the gas in question and shake it with the gas about a minute. This saturates the alcohol with methane and ethane. Run the gas out of the pipette and the alcohol up in the capillary and then pass into the pipette 100 c.c. of the carefully measured fresh gas. Shake this with the alcohol and then measure the decrease in volume after the gas has stood in the burette long enough for all the alcohol vapors to dissolve in the water. The decrease in volume is the amount of hydrocarbons higher than ethane. If there is a large amount of these, one treatment with alcohol is not enough. The writer has obtained good results in this way using gas into which had been introduced known amounts of gasoline vapors, petroleum ether vapors and benzene vapors.

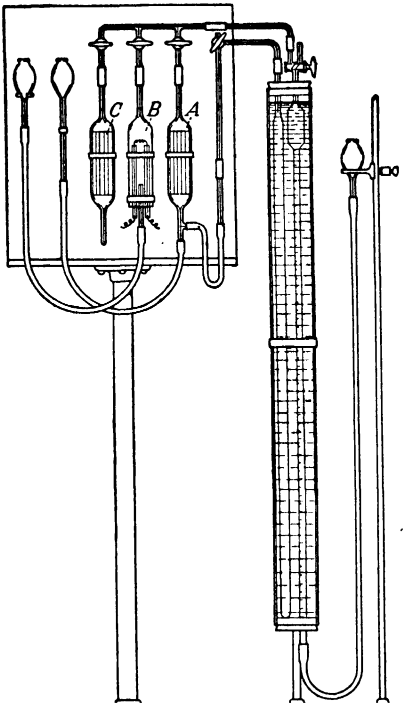

FIG. 27.

The calorific values of gases may be very accurately calculated from the analysis, using the data given in the table on page 447, remembering that the analyses of the gas are always on the dry basis (page 322).

When extreme accuracy is necessary in the analysis of gases by the above methods, it is necessary to use somewhat different apparatus, which always involves the use of a compensator attached to the burette and the burette must be graduated to 0.01 c.c. The apparatus shown in Fig. 27 is the one devised by George Burrell of the Bureau of Mines. For further particulars, see *J. Eng. Chem.*, Vol. IV, No. 4.

When highly accurate analyses of gases containing more than very small amounts of hydrocarbons (paraffin) other than methane and ethane are necessary, the sample must be treated by refrigeration analysis as described in Bulletin *Technical Paper* 104 of the U. S. Bureau of Mines by Burrell, Seibert and Robertson.

THE ANALYSIS OF MINE AIR

This may be done with the above-mentioned apparatus of Burrell or Haldane or by the use of the Hesse apparatus here described, or by the Hempel apparatus. The results are very accurate.

The titration method for mine air analysis is especially good on account of the very large sample which can be used and the simplicity of the apparatus.

The CO_2 is determined by absorbing it in a standard $Ba(OH)_2$ solution, the excess of $Ba(OH)_2$ being titrated by a standard oxalic acid solution.

The methane is burned to CO_2 by means of a yellow hot platinum wire, and the CO_2 produced is determined as above indicated.

Solutions Required.—A barium hydroxide solution made by dissolving 15 grams $Ba(OH)_2.8H_2O$ and ½ gram of $BaCl_2$ in water and diluting to a liter. The reaction with CO_2 is

$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O.$$

One liter of CO_2 at 0°C. and 760 mm. pressure weighs 1.965 grams, and the amount of $Ba(OH)_2$ to be dissolved in a liter is calculated thus, $315.5:44::x:1.965$. $x = 14.09$. This would, theoretically, require 14.09 grams $Ba(OH)_2.8H_2O$ in a liter, so that 1 c.c. would equal 1 c.c. of CO_2 at 0°C. and 760 mm. pressure, but the $Ba(OH)_2.8H_2O$ is never pure. The $BaCl_2$ is added to make the end point with phenolphthalein sharp by decreasing the ionization of the BaC_2O_4 formed during the titration.

An oxalic acid solution, 1 c.c. of which equals 1 c.c. CO_2, is used as a standard. Oxalic acid can be obtained pure. It consequently is made of exactly the right strength and the $Ba(OH)_2$ solution is standardized against it. The reaction is $Ba(OH)_2 + H_2C_2O_4 = BaC_2O_4 + 2H_2O$. One molecule of oxalic acid is therefore equivalent to one of CO_2 and the amount of oxalic acid required in a liter of solution, so that 1 c.c. = 1 c.c. CO_2 is calculated thus (the formula of crystallized oxalic acid being $H_2C_2O_4.2H_2O$) 126.04:44::x:1.965. x = 5.629. Weigh this amount carefully, dissolve in CO_2 free distilled water and dilute to a liter with CO_2 free water.

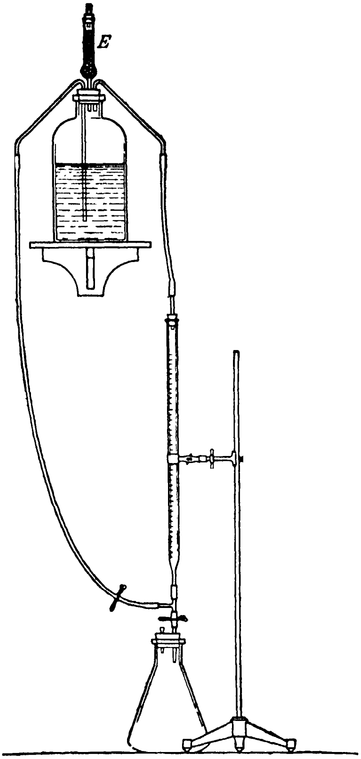

FIG. 28.

The $Ba(OH)_2$ solution should be kept in a bottle arranged as shown in Fig. 28. In this way the carbon dioxide of the air is kept from the $Ba(OH)_2$. The tube *E* contains soda lime.

The samples are taken in strong Erlenmeyer flasks of from 500 to 1,500 c.c. capacities, depending upon the amount of CO_2 and CH_4 in the mine air. The flask is calibrated by filling it with distilled water, forcing a two-holed stopper into it, wiping dry on the outside and weighing. The flask is then emptied, dried and weighed with the stopper. The difference divided by the weight of 1 c.c. of water at the observed temperature of the water is the volume of the flask.

Process of Analysis.—Place in the neck of the dry flask a paper funnel made in the shape of an ordinary glass funnel, extending nearly to the bottom of the flask. Swing the flask and funnel with the funnel mouth turned against the air in the place where the sample is to be taken. The swinging should be done 100 times to remove the air previously in the flask. Then place the two-holed stopper in the flask with plugs in the holes and take the sample to the laboratory.

On reaching the laboratory, remove the plugs and insert the tip of the $Ba(OH)_2$ burette, which should not fit tightly in the hole. Run in 10 to 20 c.c. of $Ba(OH)_2$ solution, add 4 drops of phenolphthalein solution and replace the plugs. Shake the flask frequently, and, while the CO_2 is being absorbed, standardize the $Ba(OH)_2$ solution by running into a similar flask filled with pure outdoor air the same amount of $Ba(OH)_2$ solution as was used above and shake both flasks for five minutes, without splashing up on the stopper. Then remove the plugs, insert the tip of a burette through the stopper and run in standard oxalic acid until the phenolphthalein just loses its red color. Do this to both solutions.

Suppose that 20 c.c. of $Ba(OH)_2$ solution were used in each case and that 21 c.c. of oxalic acid were required to standardize the $Ba(OH)_2$. Further, suppose that 15 c.c. of oxalic acid were used to titrate the $Ba(OH)_2$ left after absorption of the CO_2 in the sample. Then we have

21 c.c. oxalic acid $+ CO_2$ in pure air $= 20$ c.c. $Ba(OH)_2$.
15 c.c. oxalic acid $+ CO_2$ in the sample $= 20$ c.c. $Ba(OH)_2$.
CO_2 in sample $= 6$ c.c. $+ CO_2$ in pure air.

If the flasks had volumes of 1,000 c.c. each and the temperature of the sample was 20°C. and barometric pressure was 745 mm., the percentage of CO_2 in the sample would be,

$(6+0.3) \div (1{,}000-20$ c.c. displaced by $Ba(OH)_2$ solution$) \times {}^{273}\!/_{293} \times {}^{745}\!/_{760} \times 100 = 0.704$.

Pure air contains 0.03 per cent CO_2.

While the above determination of CO_2 is being made, the methane is determined in another flask the volume of which has been determined as above directed with the stopper carrying the electrode in it in the flask (Fig. 29). When the flask is brought to the laboratory the stopper in it is exchanged under pure distilled water for a stopper carrying the electrode made as directed on page 334. The stopper should also have a hole with a glass plug. It is best to stopper the flask at the place of taking the sample with the stopper having the electrode in it, then the exchange of stoppers is eliminated.

Now place the flask with the electrode reaching nearly to the bottom under a stream of water and pass through the platinum wire sufficient electric current to heat it yellow hot and continue the heating at least 15 minutes. The flask must be kept cool or the air in it will expand and burst it. Now turn off the current and determine the CO_2 in the flask, in exactly the same way as above directed. This includes both the CO_2 produced by the burning of the methane and the CO_2 already in the original sample. From this total is subtracted the CO_2 found in the same volume of the other sample and the difference is the CO_2 produced by the burning of the methane, which is the same as the volume of the methane. This volume is then figured to percentage as directed for CO_2.

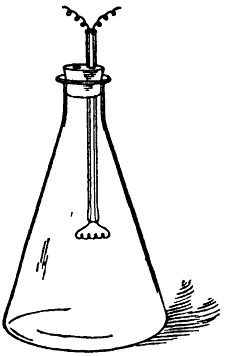

FIG. 29.

Notes on the Process.—It is best to take the samples as above directed rather than by emptying a flask filled with water, for, unless the water is very pure distilled water, it will cause error by being alkaline or acid, or containing CO_2. Moreover, the flask should not be shipped wet on the inside if many hours will elapse before the analysis is made, for the wet surface of the flask becomes alkaline.

The methane may be determined in the same flask used for the determination of CO_2, after the CO_2 titration.

It is necessary for the platinum spiral to be heated yellow hot or some methane will be unburned.

The water used when the flask is immersed to exchange stoppers *must* be absolutely neutral and free from CO_2, or error will be caused.

REFERENCES ON GAS ANALYSIS:

Bull. 42, U. S. Bureau of Mines (mine gases and natural gas).
Bull. 19, U. S. Bureau of Mines (natural gas).
Bull. 1, U. S. Bureau of Mines (coal gas).
Bull. 12, U. S. Bureau of Mines (furnace gas).
TREADWELL-HALL, "Analytical Chemistry," **2.**
WINKLER-LUNGE, "Technical Gas Analysis."
HEMPEL-DENNIS, "Gas Analysis."
WHITE, "Gas and Fuel Analysis."
Gas Chemists Handbook, Amer. Gas Association.

IODINE PENTOXIDE METHOD FOR C O

The most accurate quantitative method for determining CO in very small amounts is based on the reaction $I_2O_5+5CO=5CO_2+2I$, the CO_2 produced being absorbed in $Ba(OH)_2$ and titrated as above directed. (See *Bull.* 42, U. S. Bureau of Mines.)

The power of iodine pentoxide to oxidize CO with simultaneous liberation of iodine has been made use of in a very effective way by Hoover and Lamb in their "Hoolamite." This is a mixture of 124 parts of pumice, 124 parts of fuming sulfuric acid, containing 28 per cent free SO_3 and 102 parts of I_2O_5. This mixture is put in small glass tubes. When air containing CO is drawn through this tube, a green color is produced, the depth of which depends upon the amount of CO in the air. The device is very useful for mine air testing.

The Pyro Tannic Acid Method for the Determination of Carbon Monoxide in Blood and Air.—Messrs. Sayers, Yant and Jones of the U. S. Bureau of Mines laboratory have developed this excellent method for determining carbon monoxide in the blood of gased persons; and when present in small amounts in mine air and in similar places. The method, when used for the determination of CO in the air, has an accuracy of about 0.03 when the CO is 0.15 per cent of the air. The percentage of saturation of CO in the blood can easily be determined to an accuracy of 5 per cent.

Blood has 300 times the affinity for carbon monoxide that it has for oxygen. When blood solution is treated with a solution of tannic and pyrogallic acids, a light brownish-gray suspension is formed after a few minutes. If the blood, however, contains CO, the suspension has a carmine color, the depth of the color depending upon the per cent of CO present. Hence, by comparing the color of the blood with a set of standards, one may accurately determine the CO in the blood. The same principle may be used to determine the amount of CO in air. The standards in routine analysis are made of pigments and are permanent, but for occasional analyses it is convenient to make air mixtures containing known small percentages of CO, running from 0.2 down to 0.02 per cent. The apparatus required is:

Small test-tubes (of the same size and glass as those used for standards) for preparing the specimens of blood.

A dilution pipette for measuring blood. The long capillary stem is calibrated to a 0.10-c.c. mark, and the total pipette has a volume of 2.00 c.c. This permits the dilution of a 0.10-c.c. sample of blood with water to 2.00 c.c., or a ratio of 1 in 20.

A spring haemospast for making small puncture wounds from which the blood is obtained.

Rubber hose for wrapping the subject's finger during the taking of the blood sample.

Tannic-pyrogallic acid mixture (0.04 gram of a 1 : 1 mixture) for producing the colored suspension in the diluted specimen of blood.

Complete set of standards.

Air sample bottles of at least 250-c.c. capacity, fitted with rubber stoppers.

Rubber aspirator bulb with attached scrubber (tube of soda lime) for removing gases which might have an interfering effect.

Sampling.—Obtain the sample by inserting the glass tube on the end of the scrubber into the sample bottle, and then aspirate the air through the sample bottle long enough to purge it of its original contents—at least 25 squeezes of the bulb. The last bulb of gas should be expelled through the sample bottle while the glass tube is being removed, after which the rubber stopper should be quickly and tightly inserted. The samples can then be transported to the place for making the analysis, usually away from the place where the sample has been taken.

Blood for Making Analysis.—The blood to be used in making the analysis should be taken from a person who has not been exposed to carbon monoxide. The 0.10 c.c. of blood is diluted to 2 c.c. All of the 2 c.c. of blood solution is discharged immediately from the pipette into the sample bottle, and similarly in the bottles containing air with known small percentages of CO, say 0.04, 0.08 and 0.12 per cent.

Equilibration.—This should be done in a dimly lighted place. After replacing the stoppers, the bottles are held horizontally and rotated constantly for 15 to 20 minutes, avoiding violent shaking and agitation. As much as possible of the surface of the bottle should be covered with the blood solution. Every now and then the solution can be centrifugally thrown from the sides to the bottom of the bottle by a quick swinging motion, which allows a new surface to be formed and aids in reaching equilibrium.

Analysis.—When the equilibrating has been finished, the solutions are poured into test-tubes, the tannic-pyrogallic acid added, and the amount of CO determined by comparison with the colors of the samples containing known percentages of CO.

CHAPTER XLII

HEATING VALUE OF GAS

DETERMINATION OF SPECIAL CONSTITUENTS

The heating value of gas for industrial and municipal purposes in this country is generally given in B.t.u.'s per cubic foot of the wet gas measured at 30 in. of mercury and 60°F. This can be quite accurately calculated from the analysis as obtained by the methods already described in this chapter and by use of the tables on page 447.

It is more accurate and more satisfactory to determine the heating value in a gas calorimeter as described on the following pages:

The apparatus consists of a combustion chamber surrounded by a group of numerous copper tubes, about which is flowing a measured current of water. The heat in the products of combustion are given up to the water as they pass through the tubes. By measuring the amount of gas used, the temperatures of the ingoing and outgoing water and the amount of water which is heated we have the data for computing the heat given up by a unit volume of gas. Since 1 B.t.u. is the amount of heat required to raise 1 lb. of water 1°F., the computation is easy. For practical purposes, it is sufficient to assume that the specific heat of water is the same at all ordinary temperatures, although this is not strictly true.

The most usual source of error is due to errors incident to metering the gas, hence great care must be used in setting up and using the meter and in calibrating it.

Operation of Calorimeter.—(From Report of American Gas Institute.) Set up the apparatus as shown in Fig. 30.

Screw on the inlet water pipe and see that the air vent tube is in its place in this pipe.

Level the calorimeter by means of the screw feet and plumb-bob.

Connect the center hose nipple on the inlet weir with rubber tubing to the water supply and the side connection to the sink to carry away the overflow.

Connect the tubing for water running to weighing pail to the vertical nipple on the three-way cock on the outlet weir and for the waste to the side nipple.

Screw the 32 to 100° thermometer on the inlet water pipe and 60 to 110° thermometer on the top of the instrument for the outlet water. Screw the small thermometer in place on the exhaust flue.

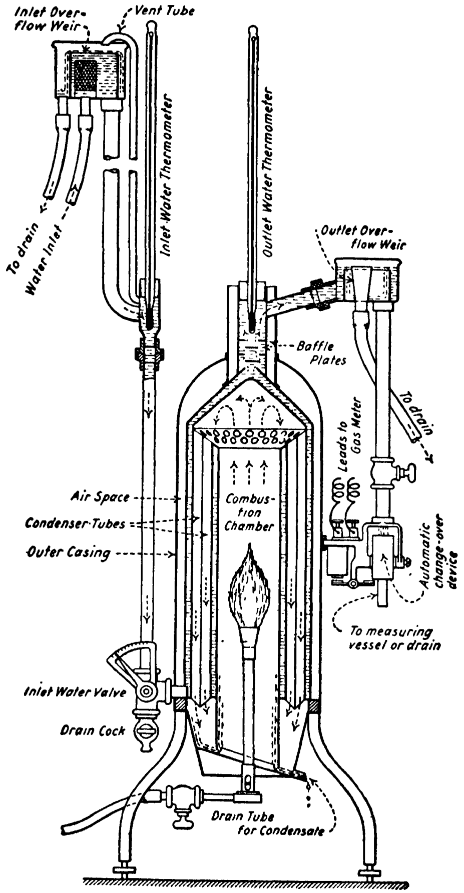

FIG. 30.

Place the two telescopic sights in position on the water thermometers, being very careful not to break them off by pressure against the sights.

Connect the meter to the governor and the governor to the burner with short pieces of rubber tubing, or with flexible metal tubing having coupled ends.

The calorimeter should be set up in a quiet, light and well-ventilated room or cabinet, which is free from drafts and in which the temperature can be maintained constantly at not less than 60°F. The room should be provided with a sink and with a good supply of running water. It is advisable to have a large shallow overhead covered tank, from which the water supply can be taken. Should the tank capacity be small and not hold enough water for a prolonged series of readings, a small gas water heater may be employed to bring the water to approximately the room temperature. It is desirable to use water that is clear and free from suspended matter in the calorimeter; therefore, a filter should be installed in the water supply line before it enters the overhead tank.

If only a single test is desired, gas may be taken from the house piping, but if an average value is required, a small gas holder, or averaging tank, should be used, and the gas flowing into the holder adjusted to a rate of flow just to fill it in the time during which the sample is to be taken. Care should be taken to have a short service to this holder in order that an average sample of gas may be obtained, and if the sample be taken from a line on which there is no considerable consumption, see that this line is thoroughly purged before sampling. It is recommended that the gas be metered at a pressure not to exceed 2 in. of water; if this is not obtainable, it is advisable to insert a holder or diaphragm governor in the supply line to reduce the pressure to within this limit.

Set up the calorimeter so that the overflow and outlet water can be easily led to the sink. Make water connections with rubber tubing, being careful not to cramp the tubing. To avoid air currents caused by the movement of the observer's body, set up the calorimeter so that the water supply and waste may be easily adjusted and all temperatures may be readily observed. Lead the outlet water to a waste funnel supported a little above the top of the copper or glass container used in collecting the water, so that the water can be shifted from the funnel to the container and back without spilling.

Set up the gas meter facing the observer and level it carefully. Then adjust the water level of the meter, both inlet and outlet being open to the air. To do this, remove the plug from the dry well, open the funnel-cock and disconnect the tubing on the outlet of the meter. Add or remove water (through the funnel or by the cock under the gage glass) until the lowest edge of the meniscus just touches the scratch on the gage glass, or is even with the fixed pointer. If the meter has been filled with fresh water, the gas must be allowed to burn at least two hours before making a test. When the water in the meter is saturated with gas, 20 minutes should be sufficient.

Fill the pressure regulator with water, about three-fourths full, then connect it to the calorimeter burner. Metallic tubing is preferable, but when rubber tubing is used to connect meter, pressure regulator and burner connections should be as short as possible, and should be saturated with the gas.

Turn on the gas and allow it to burn for five to ten minutes with the burner on the table. Shut off gas at the burner and watch, hand on meter, for leakage. Be sure that all leaks are stopped before attempting to make a test. Start water running through the calorimeter at a rate of about 3 lb. per minute. Then regulate the gas to flow at a rate of 4 to 7 ft. an hour, as may be found by experiment to give the highest result with the gas to be tested, admitting enough air through the burner so that the flame shows a faint luminous tip, then insert the burner as far up into the combustion chamber as the bracket permits, and observe again the conditions of the flame to see that it is all right, using a mirror.

The excess of air passing through the calorimeter is controlled somewhat by the position of the damper in the exhaust port, and the best results are obtained by having the excess air as low as possible and still maintaining complete combustion of the gas. To determine this position of the damper, some experimentation may be necessary. Operate the calorimeter until a thermal balance is established on the inlet and outlet water thermometers. Start with the damper closed, then open slightly, observing carefully the outlet thermometer. When this thermometer reads at a maximum—or, in other words, when the greatest rise in temperature is given to the water, which is presumably passing through the calorimeter uniformly—the damper is in approximately the correct position for the amount of gas being burned, and the excess air necessary for perfect combustion is at a minimum.

Water should be regulated so that there is a difference between the inlet and outlet temperatures of about 15°F. The temperature of the inlet water should vary but little when an overhead tank is used and the water maintained at room temperature. Be sure that both overflows are running.

Before making the test, the barometer, temperature of the gas at the meter, temperature of room and temperature of exhaust products should be recorded. It is desirable to have the temperature of the inlet water and temperature of exhaust products as nearly as possible at room temperature, in order to establish more nearly a thermal balance—the difference in these temperatures should never exceed 5°.

Next allow the gas to burn in the calorimeter until a thermal balance is established, or until there is the least change in the inlet and outlet waters.

The test may now be started by shifting the outlet water from the funnel to the container just as the large hand on the meter passes the zero point. Readings are then made of inlet and outlet thermometers, making the readings as rapidly as the observer is able to record them during the consumption, preferably of $\frac{2}{10}$ cu. ft. of gas. At least 10 readings should be made of both inlet and outlet water temperatures. Water is again shifted from the container to the waste funnel as the hand passes the zero point the second time. Water is then weighed or measured. The uncorrected heating value per cubic foot is obtained by multiplying the difference of the averages of inlet and outlet temperatures by the number of pounds of water and by dividing by 0.2. This quantity is divided by the correction factor for barometer and temperature, obtainable from tables, to give the heating value at 30 in. pressure and 60°F. The weight or contents of container should be obtained while the inside is wet. This may be done by filling it with water, emptying and shaking for about five seconds in an inverted position. This will do away with any correction where several consecutive tests are required with the same container.

A second, and perhaps third, test is advisable, and these should be made without disturbing the existing conditions, provided all readings are within the above prescribed limits. In practice, the operator should get consecutive results on the same holder of gas within 5 B.t.u. Under such conditions an average of the results may be safely taken.

Calculation.—The method of calculating the calorific value of the gas from the observations indicated is very simple when all readings are made in English units, as recommended, and entered in some form conveniently arranged.

The averages of the inlet and outlet water temperatures are determined and necessary corrections for thermometer errors are made. The difference in these averages should give the rise in temperature of the water. This rise in temperature of the water is then multiplied by the number of pounds of water passed through the calorimeter during the test.

The product of these two is then divided by the quantity of gas burned—0.2 cu. ft. This quotient will give the heating value of 1 cu. ft. of gas in B.t.u.'s. at the indicated temperature and barometric pressure. To correct this to 60°F. and 30 in. pressure, divide by the "correction factor" for the indicated temperature, and pressure as obtained from the table on page 454. The final result will be the corrected heating value of the gas tested, in B.t.u's.

Expressing the above in a formula, we have:

$$\text{B.t.u. per cubic foot} = \frac{W \times T}{G}.$$

W = weight, in pounds, of water passed.

T = the average difference in temperature, in degrees Fahrenheit, between the inlet and outlet water

G = corrected volume of gas burned, in cubic feet.

The correction for atmospheric humidity is made finally, if so desired.

To calibrate the meter, prepare a bottle holding about 40 liters with a very tight-fitting two-hole rubber stopper, through one hole of which passes a glass tube to the bottom of the carboy and through the other a tube just through the rubber stopper, weigh the carboy empty, then fill it with tap water and weigh again and determine the specific gravity of the water used. From this data calculate the volume of the carboy. Connect the carboy to the gas meter as if it were a source of gas, level and note the reading on the meter, then pass into the carboy from a water tap a stream of water so as to force the air from the carboy through the meter at the usual rate. When the carboy gets just full, stop the water and read the meter.

Corrections for Atmospheric Humidity.—(From Report of American Gas Institute.) This correction is found to be the greatest when the percentage of humidity of the atmosphere is lowest. The reason is that the relatively dry air entering the calorimeter causes to be carried out in the exhaust products a larger amount of the water in the form of a gas or vapor, which is formed by the combustion of the gas, and which does not condense, and, therefore, does not give up its latent heat to the calorimeter.

The humidity correction should correct for any discrepancy in water vapor carried in by the air and gas, compared with that carried out by the products of combustion.

Owing to the contraction in volume, during the combustion of ordinary illuminating gas and air, this discrepancy is practically nothing when the percentage of atmospheric humidity is about 80 per cent. at normal temperatures, and the excess of air introduced for combustion is about 30 per cent.

In correcting for atmospheric humidity it is assumed that the gas is saturated with water vapor—having passed through a wet meter. This assumption might not be absolutely true, but the percentage of saturation has been found always to be high, and as the volume of gas is only about one-eighth of the mixture, the error involved may be neglected.

CORRECTIONS TO OBSERVED HEAT TO GET TOTAL HEAT VALUE

(Air, gas and exhaust must be at the same temperature)
If 7 volumes of air per volume of gas are used

Humidity, per cent	65°	70°	75°	80°	85°	90°
10	+4.8	+5.7	+6.7	+7.9	+9.2	+10.5
20	+4.1	+4.9	+5.7	+6.8	+7.8	+ 9.0
30	+3.4	+4.1	+4.7	+5.6	+6.5	+ 7.4
40	+2.7	+3.2	+3.7	+4.5	+5.2	+ 5.9
50	+2.0	+2.4	+2.8	+3.4	+3.8	+ 4.3
60	+1.3	+1.6	+1.8	+2.2	+2.5	+ 2.8
70	+0.6	+0.8	+0.8	+1.0	+1.2	+ 1.2
80	−0.1	+0.0	−0.1	−0.1	−0.1	− 0.3
90	−0.8	−0.9	−1.1	−1.3	−1.5	− 1.9
100	−1.6	−1.8	−2.0	−2.4	−2.8	− 3.4

NOTE.—These corrections are expressed in B.t.u's.

The value for B.t.u's. obtained as above described is the "gross" value.

REFERENCES:

"Gas Chemists Handbook," 2nd ed.
WHITE, "Gas and Fuel Analysis."
Bull. U. S. Bureau of Standards, "Industrial Gas Calorimetry."

HYDROGEN SULFIDE

Qualitative Test.—A strip of white filter paper is dipped in a solution containing 5 per cent by weight of lead acetate, the excess solution being removed from the test paper with a clean blotter. The paper is exposed for one minute, while moist, to a current of gas flowing at the rate of approximately 5 cu. ft. per hour in an apparatus as described below, or in a similar apparatus.

The gas may be considered free from hydrogen sulfide if the paper thus exposed is not distinctly darker than another paper moistened with the same solution but not exposed to the gas.

The apparatus for exposing the paper is made from a cylindrical gas chimney 8 in. long, and 1¾ in. in diameter. The pillar of a gas burner from which the lava tip has been removed is inserted through the lower stopper, and a small glass, 1 to 1¼ in. in diameter, is supported above the pillar to prevent the gas from impinging directly on the test paper. The watch glass may be supported on three glass pegs, ½ to 1 in. high, being held in place with small bits of wax. The gas is burned from an ordinary open flame burner on the upper stopper, this burner being so selected that it will pass 5 cu. ft. per hour at the ordinary pressure of the gas supply. The test paper is hung on a glass hook so that it is held midway between the watch glass and the bottom of the upper stopper.

This apparatus may be attached permanently to a wall bracket, or a Bunsen burner may be inserted through the lower stopper in place of the pillar, so that the apparatus may be conveniently attached at any outlet with a rubber hose.

Iodine Titration for H_2S.—For works control the Tutweiler burette is the most widely used method, giving within small errors the best results and it can be recommended as sufficiently accurate for all practical purposes. The apparatus consists of a burette provided at the top with a two-way and at the bottom with a one-way cock, communicating at the top through one of the outlets with a 10-c.c. glass-stoppered cylinder graduated into $1/10$ c.c. There are only two graduations on the burette proper, one at the 100-c.c. mark, and the other 50 mm. from the bottom cock, dividing the remaining space into two divisions of about 5 and 10 c.c. respectively. A leveling bulb is attached to the lower cock, and the burette mounted on a stand.

Chemicals.—The following chemicals are necessary:

1. *Standard Iodine Solution.*—One cubic centimeter of this solution should contain 0.0017076 gram iodine, which is equivalent to 100 grains of hydrogen sulfide per 100 cu. ft. of gas. Results are reported as grains per 100 cu. ft. of gas.

2. *Starch Solution.*—Rub into a thin paste about 1 teaspoonful of wheat starch with a tablespoonful of water. Pour into a pint of boiling water, stir, allow to stand until cold and pour off the clear solution for use. Make a fresh solution every few days.

Process of Analysis.—Fill the leveling bulb with a starch solution and turn cocks so that on raising the leveling bulb the starch solution will fill the burette and run out through the gas inlet tube. Close the lower cock and attach the rubber tube through which the gas to be tested is passing to the inlet tube. Open the lower cock and lower the leveling bulb until the starch solution just passes the 100-c.c. mark on the stem of the burette. Close the lower cock, then close the top cock and disconnect from the gas supply. Open the lower cock and bring the starch solution to the 100-c.c. mark by raising the leveling bulb, then close the lower cock and open the top cock to the air momentarily to obtain atmospheric pressure in the burette. Close the top cock and by opening the lower cock and lowering the leveling bulb draw the starch out of the burette down to the 10-c.c. mark. Close the lower cock, place a clip on the rubber tubing near the bottom of the burette and disconnect the leveling bulb from the burette.

We now have 100 c.c. of gas measured at atmospheric temperature and pressure, under a negative pressure.

Fill the graduated cylinder with standard iodine solution, noting the reading on same. Admit iodine solution into the burette very gradually, shaking well between each addition. Continue until the starch solution assumes a faint but permanent blue color.

Note reading on the graduated cylinder, which, subtracted from previous reading, gives the amount of solution used. This, multiplied by 100, gives directly the number of grains of hydrogen sulfide per 100 cu. ft. of gas.

Precautions.—It will be found that, even with gas entirely free from hydrogen sulfide, an appreciable amount of iodine solution will be required to color the starch solution a permanent blue. Therefore, a certain constant, previously determined on each fresh bottle of starch solution, should be subtracted from all readings. In order to determine this constant, suck starch solution into the burette up to the 10-c.c. mark, this being the amount used in each determination, close lower cock and carefully drop into the burette iodine solution from the cylinder, shaking between each addition, until the starch solution assumes a permanent blue color. Note amount of iodine added, which will be about 0.2 to 0.3 c.c., and subtract this from the total amount of iodine solution required in each determination.

The blue color must not be confused with the opalescent milky appearance, due to the separation of free sulfur, nor with a red color, which will disappear on shaking.

For more accurate work, introduce a correction factor for temperature and pressure, bringing the gas to 60°F. and 30 in. of mercury.

When the gas contains tarry vapors a calcium chloride tube filled with cotton should be placed at the inlet to prevent tar from entering the burette.

Where a Tutweiler burette is not available, the H_2S may be determined by passing the gas—strained through cotton as above—into a solution of sodium hydroxide. This solution is acidified and titrated with iodine solution and the H_2S in a measured volume of gas calculated from the iodine used. The details of the method are as follows:

Solutions.—Sodium hydroxide of approximately twice normal strength. Hydrochloric acid of approximately twice normal strength. Starch solution made up as described under previous method, page 363. Iodine solution $\left(\frac{N}{100}\right)$, 1 c.c. of which contains 0.001269 gram iodine.

Apparatus.—Calcium chloride tube filled with cotton to remove the tar. Wide-mouth glass bottles, about 2-oz. capacity, fitted with perforated cork carrying an inlet tube extending to the bottom and an outlet tube, the bottom of which is about ¼ in. below the cork. Small wet-test meter, or a bottle equipped with a siphon to measure the gas. This bottle should be accurately calibrated and its contents should be about 0.1 cu. ft. (2,832 c.c.). Graduated glass cylinder, 25-c.c. capacity. Glass-stoppered burette, 25 c.c. graduated in 0.1 c.c. All connections should be made with pure gum tubing and the tubing before the wide-mouth bottle should be as short as possible.

Procedure.—Place 25 c.c. of sodium hydroxide in the wide-mouth bottle and connect this to the calcium chloride tube which is connected to the gas supply. Connect the outlet of the bottle to the measuring device. Allow the gas to bubble through the solution at a rate of not over 0.5 cu. ft. per hour until about 0.1 cu. ft. has passed. Shut off the gas, remove the bottle and acidify the contents with the HCl solution. Add 5 c.c. of the starch solution and drop in the iodine solution until one drop gives a blue color. The number of cubic centimeters of iodine solution used multiplied by 2.61 gives the grains of H_2S in 100 cu. ft. of the gas.

TOTAL SULFUR IN GAS

Most of the sulfur in the coal gas is present as H_2S, but small amounts—usually less than 30 grains per 100 cu. ft.—are present as CS_2 and other carbon compounds. The determination of total sulfur is accomplished by burning the gas in the presence of ammonia. The sulfur in the gas burns to SO_2, which combines with the ammonia, forming ammonium sulfite, which is absorbed in water, oxidized to sulfate with bromine and precipitated as barium sulfate. A good many forms of apparatus for accomplishing this have been used, the most common of which is the "referee's apparatus." The following description is a modification:

The apparatus is shown in Fig. 31 and consists of a burner, glass chimney, absorbing tower filled with beads and draft tube. The burner is arranged so that the glass chimney can be made to fit on it so that only enough air is admitted to burn the gas, and ammonium carbonate lumps can be placed inside the chimney in the stream of air. The bottom of the absorbing tower is open with a small drain hole, so that the condensed moisture containing ammonium sulfite and sulfate can drip into a beaker.

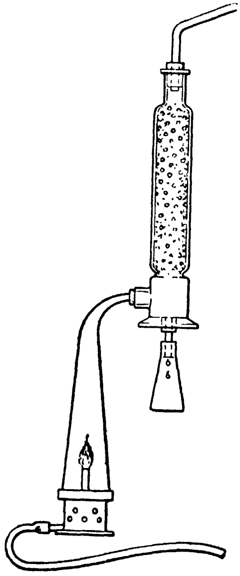

Fig. 31.

The gas which is to be analyzed should be metered in a laboratory-type wet meter, which has been previously saturated with the same kind of gas, and a pressure gage should be attached to the meter so that the results can be calculated back to standard conditions.

Procedure.—After all connections and adjustments of the apparatus have been made, the gas should be burned for several hours to saturate the meter water and to purge the connections. Before each test, the line may be purged by burning the gas for about a half hour, a burner which will pass 5 cu. ft. or more per hour being substituted for the regular test burner.

When the line is thus purged, the regular burner is put in place and ammonium carbonate placed on the burner. As much ammonium carbonate is used as will find place about the burner pillar. The ammonium carbonate should be in large lumps which have been freed from efflorescent portions. It is usually desirable to rinse out condenser and chimney tubes just before starting the test, in order to prevent the dust which might have collected there between the tests from contaminating the condensate. When all parts, including the flask to collect the condensate, are in place, the trumpet tube is set over the burner and quickly connected with the condenser, the meter reading being noted at the instant the trumpet tube is put in place. This reading and the time, meter, temperature, barometer, and manometer readings are recorded in the test record.

The gas is burned at ½ cu. ft. per hour. If the sulfate is to be determined gravimetrically, it is generally desirable to burn at least 2½ or 3 cu. ft. of gas for a test.

When it is desired to burn more than 3 cu. ft. of gas for a test, it is necessary to replenish the supply of ammonium carbonate. To do this, the gas is shut off and the trumpet tube allowed to cool so that it may be handled comfortably. A fresh supply of carbonate is then added, the burner relighted and the trumpet tube replaced quickly. If more than a few thousandths of a cubic foot of gas are burned with the trumpet tube off, the amount so burned should be deducted from the total used for the test. A fresh supply of carbonate must be added in this manner after every 3 cu. ft. of gas burned in the referee's apparatus.

When sufficient gas has been burned, the supply is cut off and the apparatus allowed to cool. The time, meter reading, meter temperature and barometer are recorded again at the close of the test. The trumpet tube is then washed once and the condenser four times. Each portion of wash water is 50 c.c. and is added all at once to flush the condenser thoroughly.

To the solution, which is diluted or concentrated to about 300 c.c., add 20 c.c. bromine water, 2 or 3 drops of methyl orange solution, heat and neutralize with HCl, adding this solution dropwise, and finally add 2 c.c. of the 1:1 acid in excess. Heat to boiling, add 10 per cent barium chloride solution, boil five minutes, allow to stand on a steam-bath for a half-hour longer, filter through a good, close-grained paper and wash with hot water until a few drops of filtrate collected in a test-tube no longer form a precipitate with silver nitrate. In a weighed crucible char the paper with low Bunsen flame and finally ignite until the precipitate appears white. Cool the crucible in a desiccator and weigh. The precipitation when made in the presence of a fixed amount of acid is always affected in equal degree by the solubility of the barium sulfate in the acid. Under the conditions given, the loss from this source is negligible for the present work. Calculate the sulfur to grains per 100 cu. ft.

The carbon disulfide sulfur is determined by subtracting the sulfur present as hydrogen sulfide from the total sulfur. It may also be determined in exactly the same way that the total sulfur is determined, except that the gas is passed through two Woulff bottles containing neutral cadmium ammonium chloride solution before the gas is burned in the apparatus. The hydrogen sulfide is removed as cadmium sulfide.

NAPHTHALENE

The amount of the hydrocarbon, naphthalene $C_{10}H_8$, usually present in gas is less than $\frac{1}{10}$ of 1 per cent. Its small amount would make it unworthy of consideration were it not for its disagreeable property of causing stoppages in gas mains. Its estimation is therefore sometimes demanded as one of the steps in controlling the manufacturing process.

The usual method for purified gas is that devised by Coleman and Smith, who based their method on Küster's method for separating naphthalene from other hydrocarbons. The method depends upon the property which naphthalene possesses of combining molecule for molecule with picric acid to form an insoluble compound. This compound is naphthalene picrate ($C_{10}H_8C_6H_2OH(NO_2)_3$).

When gas freed from tar particles, but otherwise unpurified, is to be tested for naphthalene, it must be freed from ammonia and hydrogen sulfide, which affect the titration. The gas must not be allowed to cool below the temperature of the main during this purification process, or naphthalene may deposit. However, naphthalene is nearly always determined on purified gas. Indene counts as naphlhalene.

Procedure.—Set up a train consisting of five Woulff bottles or other convenient wash bottles, followed by a gas meter and an aspirator if necessary. The connections should expose as little rubber as possible, as naphthalene dissolves in rubber. The first bottle contains normal H_2SO_4, the next bottle is empty for the purpose of catching any acid spray from the first bottle and the next three bottles contain 100 c.c. of saturated picric acid solution. Pass the gas through the train at the rate of $\frac{1}{2}$ cu. ft. per hour until 5 cu. ft. have passed through or until naphthalene picrate commences to precipitate from the second bottle.

Disconnect the picric acid bottles and transfer the solution and precipitate to a 1 liter separatory funnel, washing the naphthalene picrate with naphthalene free benzol, using about 200 c.c. in several lots. Shake the funnel until the precipitate is completely dissolved in the benzol. Reject the aqueous layer and draw the benzol solution into a 250-c.c. calibrated flask, dilute to the mark with benzol and mix well.

Titrate 50 c.c. of this solution in a 200-c.c. separatory funnel with one-fifth normal NaOH, using methyl red as indicator or, much better, using the electric resistance method for determining the end point. This titration gives the total free and combined picric acid. Since one-fifth of the solution was taken, the cubic centimeter required for titration must be multiplied by 5.

The free picric acid is now determined as follows: From a burette draw an amount of the benzol solution equal to 1,200 divided by the number of cubic centimeters of one-half NaOH used to titrate the 50 c.c. solution. The reason for using this amount is that this is the quantity which contains the right amount of total picric acid (1.1 gram) to saturate the 100 c.c. of solution to which it is finally diluted. This saturation is essential to prevent decomposition of the naphthalene picrate present at 20°C. Place this measured benzol solution in a 100-c.c. flask and evaporate to dryness to remove the benzol. To do this, put the flask on a hot water bath and pass a current of air over (not in) the benzol solution, taking care that the hot water of the bath does not reach above the level of the benzol solution. The flask should be shaken to keep the walls moistened and prevent overheating. Keep the flask in the hot water about one minute after the residue appears dry. Remove the flask from the bath but continue the current of air until the odor of benzol is gone.

Dissolve the residue in the flask with 10 c.c. of 95 per cent alcohol, heating gently if necessary, then precipitate the naphthalene picrate by adding distilled water slowly, with agitation, until the volume is exactly 100 c.c. The temperature of this solution must be cooled to 20°C.—in no case more than 2° higher or lower.

Filter through a dry filter into a 100-c.c. cylinder and titrate 90 c.c. of the filtrate with $\frac{N}{5}$ NaOH, using methyl red as indicator. Divide the cubic centimeter used by 0.9 to give the cubic centimeter required to titrate the sample taken.

Calculation of the Naphthalene.—The difference between the total picric acid in the benzol solution and the free picric acid is the picric acid combined as naphthalene picrate. Multiply the number of cubic centimeters used in the first titration by 5 and from this subtract (250÷the cubic centimeters of benzol solution taken for the second titration)×cubic centimeters calculated from the second titration. The difference is the cubic centimeter of $\frac{N}{5}$ NaOH equivalent to the naphthalene. One cubic centimeter of $\frac{N}{5}$ NaOH equals 0.0256 gram of naphthalene.

The reaction between naphthalene and picric acid is:

$$C_{10}H_8 + C_6H_2(NO_2)_3OH = C_6H_2(NO_2)_3OHC_{10}H_8.$$

One molecule of NaOH also neutralizes one molecule of picric acid.

Instead of titrating as directed above, it is more accurate to use the method and apparatus of the U. G. I. Company of Philadelphia. In this method the naphthalene is absorbed from the gas in a strong solution of picric acid, as in the old method, and then the amount of naphthalene picrate formed is determined by the change in the conductivity that occurs in the picric acid solution that has absorbed the naphthalene. This change in conductivity is due to the fact that the ionization of picric acid does not change rapidly with concentration, and when the insoluble naphthalene picrate is precipitated out, the solution becomes a poor conductor, or, in other words, its resistance rises. The method, therefore, depends upon the accurate measurement of the differences in resistance with two standard solutions of picric acid.

The apparatus, called the Naphthalene Conductivity Bridge, consists essentially of two conductivity cells, having the same conductivity constants, mounted in a Wheatstone bridge network and provided with a variable resistance so arranged that the difference in the resistance between the two solutions when the network is balanced may be read directly on a scale. Alternating current is used in order to avoid polarization effects, the ordinary 110-volt current is used and this is transformed down to 6 volts for use in the conductivity circuit. The conductivity cells are provided with thermometers to indicate the temperature of the solutions which must be closely the same, since aqueous solutions have rather high temperature coefficients.

Notes.—To absorb the naphthalene completely, the picric acid solution must be saturated, and to insure this, an excess of crystals must be present.

The benzol used may cause error and a blank should be run.

Best results are obtained when a heavy precipitate of naphthalene picrate is obtained. An appreciable quantity of naphthalene picrate should be in the first of the absorption bottles before the train is taken down for analysis. If the naphthalene content of the gas is so small that it is impossible to obtain an appreciable precipitate in the first absorption bottle, a measured amount of known solution of chemically pure naphthalene in benzol should be added and correction made for the same.

The methyl red indicator is made by dissolving 2 grams of methyl red in 1 liter of a mixture of two parts of ethyl alcohol and one part water.

In making up the absorption train, a supersaturated solution of picric acid is allowed to stand in the vicinity of the train overnight. The clear solution of picric acid is used and a very slight excess of solid picric acid is added.

The $\frac{N}{5}$ NaOH may be standardized as directed on page 61.

CYANOGEN

Cyanogen is always present in small amounts in manufactured gas. In the purification of gas most of the cyanogen is removed in the ammonia scrubbers and in the iron oxide purifiers in which the hydrogen sulfide is removed.

Cyanogen is determined by passing the gas through alkaline ferrous sulfate solutions in which the cyanogen is retained as ferrocyanide. The ferrocyanide is titrated with a standard zinc sulfate solution very similarly to the titration of zinc by standard ferrocyanide.

Procedure.—Prepare a train of four gas washing bottles or Woulff flasks, in each of the first three of which are placed 15 c.c. of 20 per cent ferrous sulfate solution and 15 c.c. of 20 per cent KOH, shaking the bottles vigorously to prevent the formation of lumps. In the fourth bottle, put 30 c.c. water. The solution should cover the dip tube at least 1 in. Pass the gas through the absorption train for three hours at a rate of 1.5 cu. ft. per hour, measuring the total amount of gas used.

Transfer the contents of the bottle to a casserole, add 50 c.c. of 20 per cent caustic potash and digest over a low flame until a test for ammonia with turmeric paper is negative. Cool the contents of the casserole, transfer to a 500-c.c. flask and dilute to 500 c.c. Mix thoroughly and filter through a dry filter into a dry beaker. Acidify a 100-c.c. portion with dilute (10 per cent) sulfuric acid, adding 10 c.c. of acid in excess and titrate with standard zinc sulfate, using 3 per cent solution of ferric alum as indicator, as in the standarization.

Standardization.—Dissolve 10 grams of pure potassium ferrocyanide in distilled water and dilute to 1 liter. Prepare a standard zinc sulfate solution by dissolving 10.2 grams of chemically pure zinc sulfate in distilled water, add 10 c.c. of H_2SO_4 and dilute to 1 liter. Measure accurately 25 c.c of the ferrocyanide solution into a 300-c.c. beaker, add 100 c.c. of water and 10 c.c. of 10 per cent sulfuric acid and 10 c.c. of saturated potassium sulfate solution. Slowly and with constant stirring add the standard zinc sulfate solution from a burette until the precipitation is complete. The end point is determined by placing a drop of the mixture on a filter paper and then placing a drop of the ferric alum solution near it, so that the two solutions spread to each other. The ferric alum solution must not touch the white precipitate in the center of the drop taken from the beaker. A blue coloration at the point where the two drops meet indicates that the ferrocyanide has not all been precipitated. When a test is obtained which does not show blue coloration at the end of a minute, the end has been reached.

Calculate the cyanogen in grains per 100 cu. ft. of gas at standard engineering conditions. One cubic centimeter of the above solution of ferrocyanide contains 0.0037 gram of cyanogen.

LIGHT OILS

Light oils is the term used to designate the benzene, toluene and xylene in manufactured gas. When gas containing these hydrocarbons is passed through the proper absorbent oil, they are retained, dissolved in the oil. Increase in weight is taken as the weight of light oils.

Procedure.—Prepare a train of ten 100-c.c. bottles with two-hole rubber stoppers. Each bottle should have the dip tube go to within ¼ in. of the bottom and the bottom of the rubber smeared with sodium silicate. In the first bottle place 100 c.c. of 30 per cent NaOH, the second bottle is left empty and to each of the other eight bottles add 65 c.c. of paraffin oil. Connect the bottles with rubber tubing, but have the ends of the glass tubes touching, wipe the bottles thoroughly with a dry towel and weigh the bottles containing the paraffin oil to the nearest $\frac{1}{10}$ gram. Connect the train to the gas main and aspirate through the train about 20 cu. ft. of gas. It is necessary usually to draw the gas through the train by means of an aspirator which, in this laboratory, consists of a 5-cu. ft. steel drum the volume of which is accurately known. The rate of aspiration should be about 2 cu. ft. per hour. The suction which the aspirator produces must, of course, be measured to correct to the standard conditions. At the end of the aspiration of the 20 cu. ft., again wipe the bottles and weigh. The increase in weight is "light oils." This is calculated to gallons per ton of coal or pounds per 1,000 cu. ft.

The train of absorbing bottles should be kept below 20°C. and the oils must be renewed for each determination. A blank should be run.

Instead of removing the "light oils" by absorption, they may be condensed in a glass-stoppered Woulff bottle immersed in carbon dioxide snow and acetone. When it is necessary to obtain enough "light oils" so that they can be distilled and the amounts of benzol, toluol and xylols can be separately determined, the apparatus described above is modified by using 2½ liter bottles containing 1 liter of oil each and aspirating about 200 cu. ft. of gas.

References:

"Gas Chemists Handbook," 2nd ed.

Chemists of the U. S. Steel Corporation, "Sampling and Analysis of Coal, Coke and By-products."

White, "Gas and Fuel Analysis."

Determination of Ammonia in Gas

When coal is carbonized, the gas which is given off contains roughly one-fourth of the nitrogen that was in the coal as ammonia. The determination of ammonia in gas is very simple and consists merely in passing the gas through a measured amount of standard acid and titrating the acid remaining at the end of the test.

Procedure.—Connect three Woulff bottles in series. In the first bottle place cotton to filter out any tar in the gas. In each of the other two bottles place 20 c.c. of half normal sulfuric acid and a few drops of methyl orange. Connect the bottle containing the cotton to the gas supply and attach an aspirator at the other end, the volume of which is accurately known. It is convenient to have a bottle holding exactly 1 cu. ft. The writer uses an iron tank which holds exactly 1 cu. ft. Draw the gas through the train at the rate of 0.5 cu. ft. per hour, and when the aspirator has drawn through the requisite amount of gas, disconnect the bottles and titrate the acid with a standard solution of NaOH until the end point becomes slightly red. One cubic centimeter of $\frac{N}{2}$ acid equals 0.0085 gram of NH_3.

The acid and alkali solutions may be standardized as directed on page 61.

The results should be calculated back to standard conditions of gas. This requires that the pressure or suction in the aspirator should be determined.

The method as above given is for purified gas. Unpurified gas contains much H_2S which dissolves in the standard acid solution and interferes with the accuracy of the end point. In this case the acid in which the ammonia has been absorbed should be made alkaline and the ammonia distilled out as directed on page 274.

CHAPTER XLIII

CHEMICAL ANALYSIS OF CLAYS, SILICATE ROCKS AND SLAGS

The methods here given are those used in the laboratory of the Department of Metallurgy of The Ohio State University for the analysis of silicates for the Geological Survey of Ohio. They are quite similar to those given in *Bulletin* 422 of the United States Geological Survey. For greater detail that bulletin should be consulted.

Natural silicates are liable to contain any or all of the following constituents: SiO_2, TiO_2, ZrO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, V_2O_5,FeO, MnO, NiO, CoO, MgO, CaO, SrO, BaO, ZnO, CuO, K_2O, Na_2O, Li_2O, P_2O_5, SO_3, CO_2, F, Cl, C, N, S, H_2O. Also, occasionally, are found boron, thorium, cerium, glucinum and, indeed, nearly any of the known elements. The complete analysis of a silicate rock is, therefore, liable to be a very complex and difficult process. Of course, for technical purposes, it is usually unnecessary to make a complete analysis, but results should be obtained as completely as possible within a reasonable cost, otherwise important data may be passed by. Whenever possible, a silicate rock analysis should be accompanied by a microscopic examination, as this often reveals the presence or absence of constituents which call for a modified procedure with a great saving of time and increased accuracy. Accurate silicate analysis can only be accomplished as the result of considerable experience.

Since many reagents are used in the separations involved in silicate analysis, they should not be used in unnecessarily large amounts, else they accumulate so greatly as to interefere seriously with accuracy. *"Blank" determinations should be made frequently*, and corrections made on the analyses of the samples.

Most silicates are insoluble in acids and must be decomposed by fusion in a platinum crucible with an appropriate reagent, usually sodium carbonate. This changes the insoluble minerals, such as quartz, feldspar, micas, etc., into new compounds of sodium, such as sodium silicate, sodium aluminate, sodium titanate, which are soluble in hydrochloric acid.

Before weighing a rock sample for analysis, it must be finely ground. Since nearly all silicate rocks are abrasive, the sample will inevitably be contaminated with some material from the grinding apparatus, such as silica from agate mortars and iron from iron mortars and grinding plates. The former is not serious but the latter is and the iron must be removed by a magnet.

Process of Analysis.—Grind several grams of the air-dried sample in an agate mortar until it no longer feels gritty under the pestle, transfer the powder to a glazed paper and rub gently through the sample a magnet, over the poles of which a piece of glazed paper has been folded. Lift the magnet and paper and clinging particles from the sample and hold over another glazed paper, remove the magnet and the magnetic particles will drop onto the paper. Repeat this process until no more particles cling to the magnet. Use the magnet on the accumulated magnetic particles to remove from them adhering rock particles which should be returned to the sample. Examine the magnetic particles with a microscope to make sure they are all bits of iron and not magnetic minerals like magnetite.

Moisture.—Weigh accurately a clean and dry platinum crucible and then add exactly 1 gram of the sample. Put the crucible and contents in a drying oven, such as is shown in Fig. 14, and dry at 105°C. for one hour, cool and weigh. The loss in weight is chiefly hygroscopic moisture. (At this time, while waiting for the sample to dry, start a phosphorus determination as explained under "Phosphorus.")

Loss on Ignition.—After obtaining moisture results, heat the crucible gently for a few minutes, then intensely over a Meker burner for half and hour, with the lid off to insure oxidation, and finally with the lid on for several minutes, cool in a desiccator and weigh. The loss in weight in the case of clays is chiefly combined water but it also is due to the removal of any carbon, some sulfur and gases, which the sample may have contained. It is called "loss on ignition." Any ferrous iron in the sample will be oxidized to Fe_2O_3, causing a gain in weight. The result is, therefore, not to be regarded as any definite single constituent.

Fusion.—Add 6 grams of the purest sodium carbonate to the sample, mix well with a stirring rod, taking care to have no material left clinging to the rod, cover with a platinum lid and heat gently at first, finally using the full heat of a Meker burner until the mass is thoroughly liquid and quiet and no undecomposed particles are visible. Usually 10 minutes in a state of quiet fusion is enough. More should be avoided, owing to the melted mass slowly attacking the platinum. Seize the crucible with a pair of tongs, remove from the heat and tip the crucible on its side, while slowly turning it so that the fusion freezes in as thin a sheet as possible on the sides of the crucible with as small an amount freezing on the bottom as possible. When cold, tap the sides of the crucible lightly to remove the cake, put the cake in a clean casserole of 250-c.c. capacity, set the crucible and lid in the casserole, fill the crucible with hot water and pour 100 c.c. more into the casserole and heat until the cake is thoroughly disintegrated. (Or fill the crucible with water as soon as cold and direct a small sharp flame from a blast lamp against the center of the bottom of the crucible for a few seconds until the cake falls off.) Lift out the crucible and lid, wash thoroughly with a jet from the wash bottle, cover the casserole with a clock glass and add carefully (to prevent frothing over) 15 c.c. of HCl (sp. gr. 1.19) by means of a pipette. Evaporate to dryness on a steam-bath or hot plate, taking care to avoid spattering as the mass approaches dryness. Allow to bake on the hot plate for some time after complete dryness has apparently been attained. Add 10 c.c. of water and 10 c.c. of HCl, heat for several minutes to dissolve any Fe_2O_3 or difficultly soluble oxychlorides which may have been formed by the baking. Add 50 c.c. of water, heat until all NaCl dissolves and filter through an ashless filter paper into a *pyrex* beaker. Wash the paper and silica with hot water until the washing is free from chloride. This will take about 15 washings. Evaporate the filtrate to dryness as before, using the same casserole for evaporation, filter through another filter paper, wash until the filtrate is free from chloride using a policeman vigorously on the casserole, place the two papers and contents in a platinum crucible, heat gently so as to smoke off the filter paper at as low a temperature as possible, raise the temperature gradually until all the carbon has been burned off, cover the crucible with a lid and ignite with the full heat of a Meker burner for half an hour, cool and weigh. The contents of the crucible is mainly silica but it is always contaminated with about a third of the titania in the sample, some Fe_2O_3, Al_2O_3 and traces of other oxides. The silica is determined by obtaining the loss in weight when it is driven off as gaseous SiF_4 as follows: Add to the crucible 1 c.c. of water, 4 or 5 drops of sulfuric acid and enough hydrofluoric acid to fill the crucible half full. Evaporate the acids under a good hood carefully, to avoid spattering, raising the temperature at the end of the evaporation high enough to drive off the H_2SO_4, finally ignite over the Meker burner for several minutes, cool and weigh. The loss in weight is silica. The residue is Fe_2O_3, TiO_2, etc., contaminating the silica.

Al_2,O_3, Fe_2,O_3, TiO_2, Etc.—Digest the small residue left in the crucible with 5 c.c. of 1:1 HCl, loosen with a policeman and transfer to the filtrate from the silica. This filtrate contains all the constituents of the sample except the silica and, in addition, about 8 grams of NaCl resulting from the solution of the sodium carbonate fusion in HCl. Add thoroughly macerated filter paper from one 9-c. m. filter and ammonium hydroxide slowly, and with stirring, until the solution, which should have a volume of about 200 c.c. is just distinctly alkaline to litmus paper. Heat to boiling for one minute, allow the precipitate to settle and filter through an 11-c. m. paper. Wash the precipitate four times with water containing ammonium nitrate made by adding to 100 c.c. of distilled water, 2 c.c. of nitric acid (sp. gr. 1.42) and 3 c.c. of ammonia water (sp. gr. 0.90). Wash the precipitate back into the beaker in which the precipitation was made, add 10 c.c. of HCl and heat until the precipitate dissolves, dilute to 100 c.c., precipitate the $Fe(OH)_3$, $Al(OH)_3$, $Ti(OH)_4$, P_2O_5, etc. with ammonia as before, taking care to use no more ammonia than is necessary to make the solution distinctly alkaline, and to boil only about two minutes, otherwise the precipitate becomes slimy and hard to filter. Filter through the same filter paper as was used before, transfer the precipitate to the paper, using great care that none remains sticking to the beaker, which it has a great tendency to do. It is best to wipe the walls of the beaker with a small piece of filter paper adding it to the rest. Wash thoroughly with the same wash solution as was used above until the washing gives no test for chloride—which will require at least 15 washings. Put the paper and contents in a platinum crucible, smoke the paper off carefully at a low temperature, raise the temperature until the carbon all burns off and, finally, ignite it with the full heat of the Meker burner for a half an hour. Cool *in a desiccator* and *weigh quickly with the lid on.* (The Al_2O_3 is highly hygroscopic after having been ignited in the presence of macerated filter paper, which makes it very porous.) The weighed material is composed of Al_2O_3, Fe_2O_3, TiO_2, P_2O_5 and possibly V_2O_5, Cr_2O_3, ZrO_2, the rare earths, some MnO and a trace of SiO_2 obtained partly from the vessels used.

Solution of Oxides.—Put 10 c.c. of 1:1 HCl into the crucible and heat on the hot plate for several minutes to dissolve Fe_2O_3. Wash the contents of the crucible into a 50-c.c. pyrex beaker, add 20 c.c. of 1:1 sulfuric acid, evaporate until the fumes of the sulfuric acid appear, cover with a glass and continue fuming the acid strongly until about 5 c.c. are left. This dissolves all of the Al_2O_3, TiO_2, etc., unless the sample is unusually high in titania, and leaves behind any SiO_2 which may have been in the precipitate. Cool, add 35 c.c. of water and heat until everything is dissolved except a little flocculent, almost transparent silica. If the dissolved matter appears sandy rather than flocculent the sample contains an unusual amount of TiO_2 or ZrO_2, which must be dissolved by fusion with $KHSO_4$ after filtration. Filter off the flocculent silica, ignite, cool and weigh and add the weight of the silica to the main body of the silica. (If the silica was sandy appearing, indicating the presence of undissolved TiO_2, etc., treat the precipitate with hydrofluoric acid as before.)

TiO_2.—Put the solution containing the sulfates of iron, aluminium, titanium, etc. into a Nessler comparison tube and into another put the same volume of water containing the same amount of H_2SO_4, add to each 3 c.c. of a 3 per cent hydrogen peroxide solution, mix well and add to the comparison tube a standard $Ti\ (SO_4)_2$ solution until the colors in the two tubes are exactly the same, mixing well after each addition of the standard. Calculate the TiO_2 in the sample from the amount of TiO_2 added to the comparison tube. If the sample were colored by the presence of iron sulfate, the comparison tube should have the same amount of iron sulfate added to it, but this is rarely needed. If the sample contains vanadium, it will vitiate the results because it gives about the same color with hydrogen peroxide as that given by titanium. The color of the solution of titanium and hydrogen peroxide is greatly weakened by the presence of minute amounts of hydrofluoric acid and large amounts of phosphoric acid which must be avoided. If the amount of titanium in the sample is more than 2 per cent, the color is so deep as to make comparison difficult and it is necessary to take an aliquot part of the solution for comparison.

Fe_2O_3.—Transfer the solution of the sample in the Nessler tube to a small beaker, add 5 c.c. of HCl and ammonium hydroxide until the solution is just alkaline, heat to boiling and filter, wash the precipitate three or four times, wash it back into the beaker in which the precipitation was made, using not more than 40 c.c. of water, add 10 c.c. of 1:1 HCl, heat until the hydroxides have all dissolved, add $SnCl_2$ solution until the iron color just disappears, then 1 drop more, dilute to 100 c.c., cool, add 10 c.c. of $HgCl_2$ solution, stir well for two minutes and titrate the *cold* solution very carefully with $KMnO_4$ solution (1 c.c. = 0.002 gram Fe) until a faint pink color appears which persists after stirring for 15 seconds. This determination of iron is very accurate. The solutions used are made up according to directions given under the "Determination of Iron in Iron Ore." Instead of the permanganate titration as above given being used, the iron may be determined by titration by dichromate, using the electrometric end point, which is very accurate. The directions for this titration are given under the "Determination of Iron in Iron Ores." The iron in clays and silicates is usually calculated to the Fe_2O_3 state, although it is undoubtedly present partly as FeO.

Phosphorus.—At the time when the moisture determination was being made a sample was started for phosphorus. The determination is carried out as follows: Fuse 1 gram of the sample in a platinum crucible with sodium carbonate in exactly the same way as fusion is made for the analysis for silica, etc., evaporate to dryness after solution in HCl in exactly the same way as the evaporation is carried out for the determination of silica, except that only one evaporation to dryness need be made. To the filtrate from the silica add 15 c.c. of HNO_3, evaporate to 25 c.c., dilute to 100 c.c., add ammonia until the solution is nearly neutral, then 3 c.c. of nitric acid, heat to 75°C., add 30 c.c. of molybdate solution slowly and with constant stirring, agitate vigorously for several minutes, allow to settle until clear (about 30 minutes), filter, wash with a 2 per cent KNO_3 solution until free from acid, as shown by testing the washing with litmus paper. Transfer paper and precipitate to a small flask, add 20 c.c. of recently boiled water and titrate with $\frac{N}{10}$ NaOH solution as directed for the determination of phosphorus in steel. The solutions used are also the same as for this determination. In the case of rocks and clays the phosphorus is reported as P_2O_5.

When the phosphorus is determined in this way, while the evaporations for silica in the main sample are being made, much time is saved.

Al_2O_3.—The sum of the Fe_2O_3, TiO_2, P_2O_5 and SiO_2 in the oxides precipitated by ammonia, when subtracted from the total weight of the oxides, gives the weight of the Al_2O_3 (plus possible traces of ZrO_2 and rare earths and some MnO, if the sample contains much). If the microscope shows much zircon, a separate determination for zirconia should be made. ZrO_2 is rarely found in clays, but is common in sandstones and many other rocks. For its determination see page 149.

CaO.—The filtrate from the aluminium, iron and titanium hydroxides contains all the CaO, MgO, ZnO and most of the MnO, BaO, SrO, NiO and CoO from the sample in solution as chlorides. The Zn, Mn, Co and Ni, if present, are separated by $(NH_4)_2S$, as follows: Make the filtrate from the iron, aluminium and titanium hydroxides acid with HCl and boil to remove all CO_2, add NH_4OH until just alkaline, then add 2 c.c. more and saturate the solution with H_2S, add 2 c.c. more of NH_4OH, heat for some time until the precipitate settles, filter and wash with H_2S water. The precipitate may be examined for its metals. MnO must be determined on a separate sample as traces always come down with the precipitate of iron, aluminium and titanium hydroxides.

Heat the filtrate to boiling, add 10 c.c. of a saturated solution of ammonium oxalate slowly and with constant stirring, digest on a hot plate for an hour, allow to settle, filter and wash with 1 per cent ammonium oxalate solution until free from chlorides. Place paper and precipitate in a platinum crucible and smoke off the paper at a low temperature, finally burning off all the carbon at as low a temperature as possible. Put the lid on the crucible and ignite intensely for 10 minutes, cool and weigh as CaO.

The purity may be determined by dissolving the CaO in a few cubic centimeters of a hot 10 per cent sugar solution and titrating the cold solution with $\frac{N}{10}$ HCl. The CaO may be contaminated by SrO and traces of MnO and MgO. If the precipitate is made from a solution containing a large amount of MgO, the CaC_2O_4 should be dissolved in HCl and reprecipitated, the filtrate being added to the main filtrate. For the separation of CaO and SrO consult U. S. Geological Survey, *Bull.* 422.

MgO.—Add to the filtrate from the CaC_2C_4 one-fifth its volume of ammonia (sp. gr. 0.90) and then add slowly and with constant stirring 10 c.c. of a 10 per cent Na_2HPO_4 solution. Continue the stirring vigorously for several minutes for the successful precipitation depends on vigorous agitation. Allow to settle for several hours, preferably overnight, filter and wash with the same ammonium nitrate wash solution used for the hydroxide precipitate above. It is necessary to wash the beaker carefully using a policeman to loosen the precipitate which tends to cling to the glass walls. If the precipitate is very large, it should be washed back into the beaker, dissolved in HCl, made alkaline with ammonia and reprecipitated. Place paper and precipitate in a crucible, smoke off the paper at the lowest possible temperature, gradually raise the temperature to burn off all the carbon and finally ignite intensely over a Meker burner for 15 minutes. Cool and weigh the $Mg_2P_2O_7$ and calculate to MgO.

For the examination of the purity of the $Mg_2P_2O_7$ see U. S. Geological Survey *Bulletin* 422. If the MnO has not all been separated by $(NH_4)_2S$, it will come down with the magnesium phosphate. It can easily be determined in this precipitate colorimetrically.

BaO.—If the sample contains much BaO, it will be chiefly in the filtrate from the magnesium, although some will have come down with the calcium, usually only traces. Make the filtrate from the magnesium phosphate acid with sulfuric acid, heat to boiling and allow to stand for several hours. If no $BaSO_4$ separates out, the sample contains not more than traces. If a considerable amount does form, it may be filtered off and weighed but accurate results can only be obtained on a sample especially analyzed for BaO.

MnO.—This is always present and must be determined on a separate sample by the bismuthate method exactly as given for the determination of manganese in iron ores low in manganese.

Total Carbon.—Determine the total carbon exactly as carbon is determined in steel by combustion. If the sample is high in sulfur, special care must be taken to assure the complete removal of SO_2 before the CO_2 enters the weighing bulbs.

CO_2.—This is determined exactly as directed for the determination of CO_2 in limestone, or for the wet combustion of carbon from iron, except that the chromic oxide must be omitted. The CO_2 comes largely from calcium, magnesium or iron carbonates.

K_2O and Na_2O.—These are determined by the J. Lawrence-Smith method. The method depends upon the decomposition at a bright red temperature of all alkali-bearing rock forming minerals by CaO with fused $CaCl_2$ as the solvent. The calcium displaces the potassium, sodium, rubidium, caesium, releasing them as highly soluble K_2O, Na_2O, KCl, NaCl, etc., which can be easily leached out of the mass along with some CaO and most of the $CaCl_2$, leaving behind the insoluble calcium aluminate, calcium silicate, calcium phosphate, calcium titanate, iron oxide, magnesium oxide, and many other insoluble oxides and salts of calcium along with most of the CaO formed by heating the $CaCO_3$ used as a reagent. The dissolved CaO is removed by ammonium carbonate, any SO_4 in solution is removed by $BaCl_2$, the excess $BaCl_2$ removed by ammonium carbonate, all ammonium salts driven off by heat and the alkalies finally weighed as KCl and NaCl. The KCl is changed to K_2PtCl_6 and the NaCl obtained by difference. The procedure is as follows:

Weigh 1 gram of the ground sample, transfer the sample to an agate mortar, add 1.5 gram of ammonium chloride and grind thoroughly until the sample is reduced to an impalpable powder. This fine grinding is absolutely necessary for accurate results. Add 8 grams of pure calcium carbonate and grind it with the rest until thoroughly mixed, place 1 gram of the calcium carbonate in the bottom of a platinum crucible, add the ground mixture, tap the crucible lightly several times on the desk to compact the mixture and cover with 2 grams more of the calcium carbonate (the ammonium chloride and calcium carbonate used must be the purest obtainable, and, moreover, a "blank" determination of Na_2O and K_2O must be run parallel with the actual determination, using the same weights and volumes of all reagents and solutions).

Place the crucible, covered with a tight-fitting lid, through a hole in a piece of asbestos board so that three-fourths of the crucible protrudes under the board, place a large porcelain crucible or 50-c.c. beaker filled with water on top of the platinum lid, heat the bottom of the crucible by the tip of a Bunsen flame about 1 in. high until the odor of ammonia is no longer detectable at the top of the crucible. The ammonia comes from such reactions as follows: $2NH_4Cl + CaCO_3 = CaCl_2 + CO_2 + H_2O + 2NH_3$. It is very essential that the heating be done slowly, so that the $CaCl_2$ is formed as completely as possible. This slow heating requires about 20 minutes. When the odor of ammonia ceases, raise the temperature and finally heat with the full heat of a Meker burner at least one hour. In case the sample is a high alkali mineral, like the feldspars, the heating should be prolonged to nearly two hours. The cooling vessel on top of the crucible should be kept filled with water, as its function is to keep the platinum lid cool to condense any sodium or potassium chloride which may volatilize. Remove the burner, allow the crucible to cool, wash the under side of the platinum lid with a jet of water into a casserole or, better, a silica dish, drop the cake out of the crucible into the same dish and wash the crucible with water. Dilute the solution to about 100 c.c. and digest the cake until it is thoroughly slaked and no hard particles can be detected with a stirring rod. If such hard particles remain, the solution should be decanted and the particles finely ground in a mortar, then digested in the main solution until thoroughly disintegrated. After the cake has become entirely disintegrated and softened, filter the solution through 11-cm. filter paper, wash two or three times with water containing 1 per cent of ammonia water, then wash back into the beaker, add 25 c.c. of water, heat and stir, filter through the same filter paper, transfer the entire mass onto the filter paper and wash with hot water until at least 15 washings have been made. Heat the filtrate, add 3 c.c. of ammonium hydroxide and 5 grams of ammonium carbonate and allow the precipitate of calcium carbonate to settle until the solution is clear. Filter through a 9-cm. filter paper and wash until the washing is free from chloride. Evaporate the filtrate in a casserole, or, better, a silica dish, to dryness, ignite until all the ammonium salts have passed off, add 10 c.c. of water and 10 drops of a 10 per cent $BaCl_2$ solution, heat to boiling, add 0.5 gram of ammonium carbonate and 2 c.c. of a saturated ammonium oxalate solution, heat until the precipitate is completely settled, filter through a small filter paper, catching the filtrate in an evaporating dish small enough to be weighed on an analytical balance. Wash the paper six times with a small amount of water each time, evaporate the filtrate nearly to dryness, add a dozen drops of HCl and continue the evaporation to dryness, being very careful to avoid spattering. When dry, ignite very cautiously to prevent the loss of chlorides by decrepitation, finally raising the temperature to a very dull red to drive off all the ammonium salts and carbonaceous matter always remaining. Cool and weigh the dish plus KCl and NaCl. Dissolve the chlorides in 5 c.c. of water and transfer to a 100-c.c. beaker, washing out the evaporating dish carefully. If the solution of the chlorides is not clear, it should be filtered into the 100-c.c. beaker and the filter paper washed, ignited and the ash weighed and subtracted from the weight of the chlorides. The difference in weight is the $NaCl + KCl$.

K_2O.—Add 3 or 4 drops of HCl to the solution and a sufficient amount (up to 12 c.c.) of a H_2PtCl_6 solution containing 30 grams of platinum per liter. Evaporate the solution on a steam- or water-bath until only a few drops remains (it should not go clear to dryness), remove from the steam bath and when cold add 10 c.c. of an 80 per cent alcohol solution. Agitate the solution for several minutes until all sodium salts are dissolved and the beautiful yellow crystals of K_2PtCl_6 remain. Pour off the alcoholic solution very carefully without allowing any of the precipitate to pass over, add 5 c.c. more of the 80 per cent alcohol solution, decant it off and repeat the washing about three times more. Place the beaker with contents on a steam-bath and allow it to remain until no odor of alcohol persists. Brush the K_2PtCl_6 onto a tared watch-glass and weigh. The weight of the K_2PtCl_6 multiplied by 0.194 gives the K_2O in the sample, and by 0.307 gives the KCl weighed. This subtracted from the total weight of chloride gives the NaCl weighed, which when multiplied by

0.526 gives the Na_2O in the sample. A better method is to filter and wash the K_2PtCl_6 on a weighed gooch crucible.

The alcoholic filtrate and the K_2PtCl_6 contain all of the platinum used and should be saved until a sufficient amount has accumulated to be recovered and prepared as H_2PtCl_6. The recovery is best carried out as follows: Put the alcoholic solution and K_2PtCl_6 in a large evaporating dish, make strongly acid with HCl, add five times as much zinc as there is platinum present and evaporate to a small volume. Filter off the precipitate of platinum and impurities and test the filtrate with more zinc to see that the recovery is complete. Wash the precipitate of platinum into a beaker, add water and HCl and more zinc and digest to make sure that all of the K_2PtCl_6 has been decomposed, filter again on the same filter paper, wash thoroughly with water until no test for chloride can be obtained, detach the platinum from the paper and dry it, burn the paper, add the ash to the platinum and heat until thoroughly dried. Weigh, dissolve the platinum in aqua regia, evaporate to a small volume, taking care that no dry salts are formed on the side of the vessel, add a large volume of HCl and evaporate again and repeat the addition of HCl and evaporation about five times to make the removal of nitric acid complete, dilute to the proper volume so that a liter of the solution has 30 grams of platinum.

A direct check of the amount of Na_2O may be made by evaporating the solution of Na_2PtCl_6 and H_2PtCl_6 with mercury, heat to expel all the mercury, filter off the platinum, evaporate the NaCl to dryness and weigh.

In case the sample contained lithium it will be counted as sodium unless it is separately determined. This is done by Gooch's method, taking advantage of the insolubility of the chlorides of sodium and potassium in amyl alcohol in which lithium chloride is soluble.

Notes on Silicate Analysis.—The above methods are quite accurate and for technical purposes may sometimes be shortened. There are, however, some small errors to be corrected for in exact work.

The loss on ignition includes hygroscopic water, combined water, carbon dioxide from carbonates, organic matter, sulfur, oxygen from MnO_2, while the sample may take up oxygen by oxidation of ferrous iron, etc. (For a full discussion see U. S. Geological Survey, *Bull.* 422.)

When evaporations are made in porcelain casseroles and precipitations in glass beakers, a milligram or two of SiO_2 and Al_2O_3, etc., will be obtained from them. To get exact results a blank must be run.

If the sample contains fluorine, some silica will be lost as tetrafluoride.

The precipitate of iron, aluminium and titanium hydroxides will generally be contaminated with a small amount of manganese, always with one or more milligrams of silica, all the phosphorus in the sample, vanadium, if it be present, chromium, zirconium, etc. For exact work, these must be determined in the precipitate. Sometimes a sample of clay or slag may have several per cent of P_2O_5, which should be determined as in an iron ore.

The use of macerated filter paper makes the filtration of a large precipitate of $Al(OH)_3$ much easier, and also greatly aids the subsequent solution of the ignited precipitate. In fact, it is easily soluble in 1: 2 sulfuric acid.

When iron is reduced, there should be not more than 2 or 3 per cent of sulfuric acid present.

The precipitate of $Al(OH)_3$, etc. must be washed with an ammonium salt, not pure water. Clays always contain at least traces of titania.

The precipitate of calcium oxalate is generally contaminated with a small amount of aluminium hydroxide, iron hydroxide, magnesia, sodium and strontium. To remove these (except strontium) the precipitate is ignited, dissolved in HCl, made alkaline with ammonia, boiled, aluminium filtered off and the calcium precipitated again.

The precipitate of magnesium phosphate is likewise apt to be contaminated with barium, calcium, manganese, alumina, etc., and, unless two precipitations are made, the precipitate is apt to contain too much ammonium phosphate and be too heavy. Manganese may be determined colorimetrically in the precipitate.

In the alkali determination, especial care must be taken to make sure that the heat is not so high at first as to drive off the ammonium chloride instead of breaking it up to form $CaCl_2$ and ammonia.

Glazes.—These may contain easily reducible metallic oxides such as PbO, SnO_2, As_2O_3, Sb_2O_3, which would be reduced during fusion with Na_2CO_3 by the reducing gases present. The reduced metals will alloy with the platinum and ruin the crucible. The following method is satisfactory if carefully followed.—Fuse 4 grams of Na_2CO_3 in the platinum crucible then cause it to form a shell in the crucible by tipping and turning the crucible while the liquid is freezing. Grind 1 gram of the finely ground sample intimately with 3 gms. of

Na_2CO_3, 3 gms. of K_2CO_3 and 1 gm. of KNO_3, put the mixture in the Na_2CO_3 lined crucible, put the crucible in a muffle and very gradually raise the temperature until the mixture shows signs of melting but the Na_2CO_3 lining does not. Keep at this temperature for at least one hour. Then dissolve and proceed as usual.

If the glaze contains arsenic it should be precipitated with H_2S before evaporation for SiO_2 otherwise arsenic chloride will be lost by volatilization. This is also true of tin and antimony. The arsenic and antimony are volatile as the "ous" compounds and the tin when in the tetravalent state.

Boric oxide is determined by volatilization. See Scott "Standard Methods of Chemical Analysis," p. 82.

ANALYSIS OF BLAST-FURNACE SLAGS

The slags made in the iron blast furnace are essentially silicates of lime, magnesia and alumina. They usually contain, however, small percentages of iron, manganese and sulfur. Phosphorus is rarely present in more than traces. Titanium and other rarer elements, if present in the ore, will be found in the slag. Slags that are high in alumina and magnesia will sometimes contain small crystals of spinel ($MgOAl_2O_3$). As this substance is neither attacked by HCl, decomposed by fusion with Na_2CO_3 nor dissolved by HF, it will be found in the silica obtained in the analysis. Spinel can be decomposed by prolonged treatment with hot H_2SO_4 diluted with its own volume of water.

Most furnace slags can be decomposed by treatment with HCl, especially if they have been suddenly cooled from the molten state. Slags which are not decomposed by HCl must be fused with Na_2CO_3.

Slags frequently contain metallic iron in small grains; this should be taken out of the crushed sample by a magnet. If the slag itself is magnetic, the metal grains can be picked out under a magnifying glass with pincers. The sample must finally be ground in an agate mortar to an impalpable powder.

The exact analysis of slags is carried out the same as the analysis of silicates, as given above. If the slag has much manganese, the first precipitation of alumina and ferric hydroxide must be made by the basic acetate method, otherwise they will retain considerable manganese.

If the slag is soluble in HCl, the fusion with sodium carbonate is unnecessary.

Short Method.—For the purpose of furnace control, it is usually sufficient to know the percentages of silica, alumina, lime and magnesia in a slag. These can be determined with sufficient accuracy by the following process.

The Determination of the CaO and the MgO.—Weigh 1 gram of the sample into a casserole, add 30 c.c. of water and stir the slag up into it to prevent caking and the separation of gelatinous silica on the addition of acid. Now add 20 c.c. of HCl and heat. Everything should dissolve except a few flakes of SiO_2 and possibly a little carbon or sulfur. There should be no gritty residue. Cover the casserole, and boil the solution to dryness to separate most of the silica.

Now add 10 c.c. of HCl, a few drops of HNO_3 and then 50 c.c. of water. Boil to dissolve the bases and then transfer the contents of the casserole, without filtering, to a 500-c.c. graduated flask. Dilute the liquid to about 300 c.c. and add NH_4OH until the alumina separates, but avoid a large excess. If the sample contains more than a few tenths per cent of manganese, add 2 or 3 c.c. of ammonium sulfide to precipitate it with the alumina. Heat the contents of the flask to boiling and boil for three minutes. Cool the liquid and dilute it to the mark with water free from CO_2. Mix the contents of the flask thoroughly and then filter off 250 c.c. through a dry filter.

Determine the lime and magnesia in this volumetrically, as in a limestone. If ammonium sulfide was used, add HCl to the filtered solution till it is neutral, and then about 5 c.c. in excess. Boil till the H_2S is expelled, then add 0.5 gram of $KClO_3$ and heat till the separated sulfur is dissolved. Now add NH_4OH in excess and proceed with the determination of the lime as before. Should a trace of MnO_2 separate on adding the ammonium hydroxide, continue the heating till it dissolves and the solution is nearly colorless, before precipitating the lime.

The Determination of the SiO_2 and the Al_2O_3.—Weigh 0.5 gram of the sample into a casserole, treat it with water and HCl and evaporate to dryness as before, in this case, however, the dry residue must be heated till all HCl is expelled, avoiding a temperature of over 120°.

Take up the residue in water and HCl, filter and weigh the silica. It is well to evaporate the solution to dryness a second time before filtering off the silica, as this makes the filtration more rapid.

The residue is usually taken to be silica but is liable to contain traces of Fe_2O_3, TiO_2 and spinel. It may be tested with HF and any fixed residue deducted (see page 378). If this is done, the silica should be separated by a double evaporation, as it is not all precipitated by a single one. Ordinarily, the impurities present will about balance the silica lost and so the gross weight is nearly correct.

The alumina is now determined in the filtrate from the silica. In the absence of much manganese, this can be done by precipitation with NH_4OH, as in the analysis of a limestone, taking care to have plenty of NH_4Cl present and to redissolve the first precipitate, which is likely to contain a little lime. The precipitate should be washed by decantation until free from chlorides and then transferred to the filter. The precipitate contains all iron, phosphoric acid and titanic acid in the slag.

If the slag contains much manganese, the alumina must be separated from it by a basic acetate precipitation, as described on page 72. The precipitate is then redissolved in HCl and the alumina, now free from manganese, precipitated with NH_4OH. A double precipitation with NH_4OH accomplishes the same.

Determination of Al_2O_3 as Phosphate.—Dilute the filtrate from the silica in a 300-c.c. beaker to about 200 c.c. To the cold solution add about 15 c.c. of a saturated solution of sodium phosphate, and then NH_4OH cautiously and with constant stirring until a slight permanent precipitate forms. Now add 5 drops of HCl, which should dissolve the precipitate and leave a clear solution. Then add, with constant stirring, 20 c.c. of a saturated solution of sodium thiosulfate. If much iron is present, as in the case of an ore, the solution will turn nearly black, but, on continuing the stirring, will grow lighter as the iron is reduced and finally a white precipitate of $AlPO_4+Ti_3(PO_4)_4$ will be thrown down mixed with a large quantity of S. Cover the beaker and heat the solution till it boils. When boiling, add 20 c.c. of a solution consisting of 100 grams of sodium acetate, 200 c.c. of acetic acid (sp. gr. 1.04) and water to make 500 c.c. Boil the solution 10 minutes longer, or until the precipitate coagulates.

Let the precipitate settle, filter and wash the precipitate 10 times with hot water. Put the wet filter into a crucible, ignite at a low heat to burn off the paper and sulfur, and then ignite over the blast lamp.

The residue is $AlPO_4+Ti_3(PO_4)_4$ and contains 0.418 Al_2O_3, if Ti is absent.

REFERENCE:

J. M. CAMP, *Iron Age*, **65**, 17.

When this method is applied to ores the first precipitate is likely to contain a little iron. This can be removed by dissolving and reprecipitating it in the same way.

Sulfur and iron can be determined in slags as in iron ores.

Sulfur.—The sulfur in slags is present almost wholly as calcium sulfide. It can be determined approximately by adding 150 c.c. of water to 0.5 gram of the very finely pulverized slag and titrating with the standard iodine solution used for sulfur in iron.

Stir the mixture of slag and water and add 3 or 4 c.c. of starch solution, then run in the iodine till the blue color develops. Now add 15 c.c. of concentrated HCl, stir and add the iodine again until the color no longer disappears.

If 1 c.c. of the iodine equals 0.0005 gram S, each cubic centimeter taken will be equivalent to 0.1 per cent sulfur in the slag.

REFERENCE:

J. Anal. App. Chem., **7**, No. 5.

It is probably more accurate to evolve the H_2S in a flask as for pig iron. Put 5 grams of granular zinc into the flask, then add 0.25 to 0.5 gram of the very finely ground slag. The hydrogen from the Zn carries over the H_2S from the slag. This is absorbed by an ammoniacal cadmium solution and titrated as usual. (See CAMP, "Methods of Analysis in the Laboratories around Pittsburgh," 2nd ed.)

Manganese in slag can be determined as in iron ores. Small percentages are best estimated by the bismuthate method.

DETERMINATION OF SILICA, ALUMINA, LIME AND MAGNESIA IN IRON ORES

Silica.—Put 2 grams of the ore in a 12-cm. porcelain dish with cover; add 30 c.c. of strong hydrochloric acid and heat for half an hour, or until the action of the acid has ceased, but do not allow the acid to boil. Cool the solution for a few minutes, dilute to twice the volume with hot water and filter into another dish. Wash the residue with hot water until the water runs through colorless, ignite the filter and residue in a platinum crucible and fuse the impure silica with about five times its own weight of Na_2CO_3. When the fusion has become tranquil, place in it a stout piece of platinum wire about 8 cm. long, with the end that is put into the crucible flattened and bent at right angles; incline the crucible slightly, then remove the heat and hold the wire in position, touching the bottom of the crucible, until the mass solidifies. Now heat the crucible rapidly and uniformly with the blast lamp or Bunsen burner; lift out the melt with the wire as soon as it is loose, and place it in the dish in which the ore was first treated. Cover the dish, add about 30 c.c. of hot water to disintegrate the fusion, then add hot water to the crucible and dislodge adhering substance as completely as possible with a glass rod. Add the washings from the crucible to the main portion in the dish, and acidify the whole with 15 c.c. of strong hydrochloric acid. Cleanse the crucible thoroughly by warming a little hydrochloric acid in it, and when the solid matter is completely disintegrated, scrub the crucible with a policeman, and rinse again. Evaporate the solutions in both dishes to dryness, and continue to heat for an hour at about 120°C. Add to the dish containing most of the iron 15 c.c. of strong hydrochloric acid, and warm until the ferric oxide is dissolved. To the other dish, containing most of the silica, add just enough dilute hydrochloric acid to moisten the residue and warm, then add about 30 c.c. of hot water and boil. Pour the solution from this dish into the other dish, keeping back most of the silica, filter the contents of both dishes into a 200-c.c. graduated flask, wash both dishes carefully, using a rubber-tipped rod to remove adhering matter, and wash the filter free from chlorides. Set aside the filtrate for the determination of alumina, etc. Ignite the residue, and weigh as impure SiO_2. Add 2 drops of sulfuric acid, 10 c.c. of HF, evaporate to dryness, ignite and weigh The loss is SiO_2.

For exact results, two evaporations to dryness are necessary. Otherwise, the SiO_2 will be slightly low.

Clean the residue out of the crucible with a few cubic centimeters of HCl, using a policeman, and add the solution to the filtrate from the SiO_2.

Alumina.—The aluminium and iron are first separated from the manganese and other bases by the basic acetate precipitation; the resulting hydroxides are dissolved with hydrochloric acid, and the aluminium is separated from the solution as phosphate. Having cooled the filtrate from the silica in the flask and made the solution up to the mark, transfer one-half of the solution to a 600-c.c. beaker. Add 10 c.c. of strong hydrochloric acid; heat to boiling, cool, add NH_4OH until a very slight, permanent precipitate forms, while the solutions remain slightly acid, then add 25 c.c. of 20 per cent ammonium acetate solution; dilute to about 450 c.c. with hot water; boil for one minute and allow to stand until the precipitate settles. While heating the liquid, stir it frequently to prevent "bumping," and turn down the flame as it begins to boil. When the precipitate has settled, decant and filter the liquid through a 10-cm. ribbed funnel with the paper cut to fit. Rinse the beaker once, and wash the precipitate three times with hot water. Save the filtrate for the determination of manganese, etc. Place the beaker in which the precipitation was made under the filter and dissolve the precipitate with hot hydrochloric acid (1:1) and wash with hot water, making up the volume of the solution to about 300 c.c. Add to the solution 30 c.c. of saturated ammonium phosphate, then add NH_4OH until a slight precipitate appears, and dissolve this with a few drops of hydrochloric acid. Now add to the clear solution 50 c.c. of 10 per cent sodium thiosulfate solution; stir until a white precipitate forms, place the beaker over a flame, and just before the liquid begins to boil add 12 c.c. of ammonium acetate and 8 c.c. of strong acetic acid. After boiling for 10 minutes, filter the liquid rapidly, keeping the precipitate covered with the liquid. Wash the filter and precipitate with hot water until free from chlorides; ignite in a porcelain crucible and weigh as $AlPO_4$. Titania, if in the ore, will contaminate the $AlPO_4$. Two precipitations are necessary for the best results.

Manganese.—From the filtrate from the basic acetate separation of the iron and aluminium, precipitate the manganese as directed under the acetate method for manganese. If the precipitate is small, it should be washed well and the manganese determined in it by the bismuthate method.

With ores containing as much as 2 per cent of manganese, a double precipitation of iron and aluminium hydroxides should be made.

Lime and Magnesia.—Concentrate the filtrate from the manganese determination to half its volume, add 15 c.c. of ammonium oxalate solution, and NH_4OH until alkaline, and heat just below the boiling point until the precipitate settles readily. If there is no immediate precipitation, concentrate the solution to about 100 c.c., before adding the NH_4OH; boil for 15 minutes and filter. Wash the precipitate free from chlorides, ignite to constant weight with the blast lamp and weigh as CaO.

Cool the above filtrate; precipitate the magnesia by adding 10 c.c. of sodium phosphate solution and 10 c.c. of NH_4OH, stir well and set aside for 12 hours. Filter on a 9-cm. paper; wash with the ammonia and ammonium nitrate solution; ignite at the lowest temperature necessary to burn off the paper, and weigh as $Mg_2P_2O_7$.

If an accident happens to any of the above determinations, use the other half of the filtrate from the silica for another analysis.

PHENYLHYDRAZINE METHOD FOR ALUMINA

The alumina may be determined as follows: Dissolve several grams of the ore in HCl and filter, ignite the residue, decompose it with HF, evaporate to dryness with a drop of H_2SO_4, dissolve in HCl and add to the main solution. Dilute to 250 c.c., nearly neutralize, and reduce the iron with NH_4HSO_3. If the solution turns deep red (ferric sulfite), it is not acid enough, and a few drops of hydrochloric acid should be added, for the sulfite itself does not reduce ferric salts, at least not with rapidity. Now quickly bring to neutrality with ammonia, and then add several drops of dilute hydrochloric acid. If this last operation is done too slowly, the oxygen of the air helps to form a little ferric hydroxide, which does not always readily dissolve in the dilute acid. Finally, add from 1 to 3 c.c. of phenylhydrazine, according to the weight of the alumina to be precipitated. If too little has been used, a few drops added to the filtrate will disclose the mistake.

Stir until the precipitate has become sufficiently flaky and allow to settle. The supernatant liquid will now be plainly acid to litmus. One need not be disturbed if the precipitate has a brownish color, for it is not due to ferric hydroxide, but to the coloring matter contained in all phenylhydrazine which has not been freshly distilled. When the determinations are allowed to stand too long, the air increases this oxidation product, and a brown insoluble scum forms on the surface of the liquid and on the sides of the vessel, which is rather troublesome to the analyst. Fortunately, equilibrium appears to be established in a short time. The vessels need not stand more than an hour, at any rate. The precipitate is washed by a solution of phenylhydrazine sulfite made by adding cold saturated sulfurous acid to a little phenylhydrazine until the crystalline sulfite first formed dissolves in the excess. The solution has an acid reaction. Of this 5 to 10 c.c. are used in 100 c.c. of hot water.

Ignite the precipitate and weigh the Al_2O_3, TiO_2, P_2O_5 and V_2O_4 if present. Determine the TiO_2, P_2O_5 and V_2O_4 and obtain the Al_2O_3 by difference.

CHAPTER XLIV

DETERMINATION OF GOLD, SILVER AND PLATINUM IN ORES AND ALLOYS

These metals occur in ores as the free metals. Silver is found also as argentite (Ag_2S), proustite ($3Ag_2SAs_2S_3$), pyrargyrite ($3Ag_2SSb_2S_3$), cerargyrite ($AgCl$) and a number of other minerals. Gold does not form so many minerals as silver, the chief ones, beside native gold, being sylvanite ($AuAgTe_4$), calaverite ($AuTe_2$) and other tellurides. Platinum occurs almost exclusively as the elementary metal alloyed with other of the noble metals. Its only mineral compound is the mineral sperrylite ($PtAs_2$).

These noble metals occur usually in what is, chemically speaking, mere traces. An ore containing ½ oz. of gold per ton would be considered rich.

They are almost always determined by the methods of "fire assaying," although sometimes it is convenient to combine wet methods with dry methods.

Fire assaying consists in producing two immiscible liquids at high temperatures, one of which is molten lead and the other is a molten slag. In the molten lead the noble metals are extremely soluble, while they are not soluble in the molten slag. In the molten slag all of the oxidized minerals of the ore are soluble, while they are insoluble in the molten lead.

In order that the noble metals may dissolve in the molten lead, they must be freed from their compounds in intimate contact with metallic lead. In order that the gangue materials of the ore may be easily dissolved in the slag, they must be combined with the proper fluxes which produce compounds easily soluble in the molten slag at moderate temperatures.

The reduced metallic particles, being denser than the slag, settle to the bottom of the crucible if sufficient time is given. The lead, which has a high affinity for oxygen, is separated from the noble metals, which are not oxidizable by "cupellation," which is a process of oxidation at about 960°C.

The methods of fire assaying give extremely accurate results when due account is taken of certain losses and proper corrections made.

These losses result from a very slight solubility of the metals in the slag and from the vaporization of the metals during reduction and cupellation and absorption in the cupel. It is necessary to determine the extent of these losses and make proper correction.

There are two general methods of conducting fire assay, namely, the crucible method and scorification method. The crucible method is also carried out in two distinct ways, the excess litharge process and the excess iron processs. Litharge (PbO) is always added in the crucible assay, the reduction of the litharge to metallic lead in intimate contact with the ore being necessary to collect the noble metals and precipitate them to the bottom of the crucible, where they finally collect as a lead button which should weigh about as much as the ore used. In addition to this function, the litharge acts as an oxidizing agent to decompose the sulfides, arsenides, etc., thus liberating the noble metals, and it further acts as a flux to make an easily fusible slag. If the ore contains a large amount of sulfide minerals, such as pyrite, chalcopyrite, sphalerite, etc., the litharge is reduced to lead in excessive amount. Hence, high sulfur ores either are roasted before assaying or an excess of litharge over the amount necessary to furnish the proper sized button is not used.

When the ore contains a large amount of sulfides, the sulfur is either removed by roasting, as mentioned above, previous to assaying, or the excess iron method is used. If the ore is roasted, the excess litharge process may be used. When the ore is not roasted, the sulfide minerals are decomposed by using in the crucible mixture a sufficient amount of metallic iron (usually about four 20-penny cut nails). Since the metallic iron reduces litharge when iron is used, only enough litharge can be used in the charge to supply the necessary amount of lead to collect the noble metals and make proper sized button. The decomposition of sulfides by iron may be represented by the following equations:

$$PbS + Fe = FeS + Pb.$$

The decomposition of sulfides by litharge proceeds according to the following typical reaction:

$$FeS_2 + 5PbO = FeO + 2SO_2 + 5Pb.$$

A gold or silver ore is practically nothing but rock carrying infinitesimal amounts of precious metals and varying amounts of the metallic minerals, like pyrite, chalcopyrite, galena, etc. The rock-forming minerals, such as quartz, feldspars, micas, limestones and numerous other silicates and carbonates, are infusible at the temperature at which fire assaying must be conducted. It is necessary, therefore, that the proper amount and kind of fluxes should be added to combine with these rock-forming minerals and produce a mixture of compounds which is fusible at assaying temperature. The common fluxing materials are sodium carbonate, borax and litharge. Sodium carbonate melts at 852°C., borax ($Na_2B_4O_7$, when dehydrated) melts at 878°C., litharge melts at 888°C. The sodium carbonate combines with silicates to form sodium silicate, sodium aluminate and other similar compounds, and litharge similarly forms lead silicate. These silicates, aluminates, titanates, phosphates, etc. are soluble in a molten mixture of sodium carbonate, borax and litharge, or in molten sodium carbonate or borax alone. Hence, the addition of sodium carbonate, borax or litharge to an ore changes the rock-forming minerals of the ore to more easily fusible compounds which, in turn, are completely soluble in a fused excess of these fluxes, provided they are present in sufficient amounts. The primary function of assaying, which is to make two immiscible liquids, in one of which (the slag) the gangue materials are held liquid and in the other (molten lead) the precious metals are dissolved, is thus accomplished.

A slag suitable for assay purposes should have the following properties:

1. It should have a comparatively low formation temperature readily attainable in assay furnaces. It should approximate a monosilicate, to sesquisilicate.
2. It should be pasty at and near its formation temperature, to hold up the particles of reduced lead until the precious metals are liberated from their mechanical or chemical bonds and are free to alloy with the lead.
3. It should be thin and fluid when heated somewhat above its melting point, so that shots of lead may settle through it readily.
4. It should have a low capacity for gold and silver, and should allow a complete decomposition of the ore by the fluxes.
5. It should not attack the material of the crucible too violently.
6. Its specific gravity should be low, to allow a good separation of lead and slag.
7. When cold, it should separate readily from the lead and be homogeneous, thus indicating complete decomposition of the ore.
8. It should contain all the impurities of the ore and should be free from the higher oxides of the metals.
9. Except in the case of the iron-nail assay, it should be free from sulfides.

After the separation is complete, the contents of the crucible are poured into a mold and allowed to freeze, and, when cold, the slag is knocked off of the lead button. When this lead button is placed upon a "cupel," made usually of bone ash, and heated at about 960°C. in a muffle with an oxidizing atmosphere, the lead oxidizes and the PbO thus formed is absorbed in the cupel, finally leaving a little button of the precious metals.

This button, containing gold and silver and platinum metals if present, is treated with nitric acid (after weighing), which dissolves the silver and leaves the gold which is weighed.

The scorification assay, mentioned above, is almost the same as cupellation, being purely an oxidizing process. The material to be assayed is mixed in a scorifying dish with a sufficient amount of granulated lead which oxidizes in the muffle, and the PbO so formed combines with the gangue materials and base metals and forms with them a slag, leaving behind, finally, a lead button containing the precious metals. This lead button is cupeled as usual. The scorification assay is particularly useful in assaying alloys and ores containing large amounts of sulfides, arsenides or antimonides of the difficultly oxidizable base metals, particularly copper, nickel and cobalt and mattes, speiss and bullion. This method is not used much for gold ores, except concentrates.

System of Weights.—In this country the "assay ton weights" are used. One ton of 2,000 lb. avoirdupois contains 29,166 troy oz. If, then, a sample of 29.166 grams of ore is used, each milligram of precious metal obtained in the assay is equivalent to 1 troy oz. of metal per 2,000 lb. of ore. Sets of "assay ton weights" are made for use by assayers for convenience in weighing. An assay ton weight weighs 29.166 grams and the fractional weights are based upon this unit.

Balance.—The weights of precious metals obtained in fire assaying are sometimes very minute. Most gold ores which are mined in large quantities contain less than $5 worth of gold per ton. Since an ounce of gold is worth $20.64, this means that the weight of gold obtained from an assay ton of such ore is about 0.00025 gram and it must be weighed so that the error in weighing is equivalent to less than 20 cents per ton, or 0.00001 gram. Hence, the balance used must be extremely delicate and sensitive and used with great care. Put the balance into action by gently lowering the beam on the knife-edges. It may then start swinging slightly of its own accord. If it does not, set it swinging by gently fanning one pan with a motion of the hand, or by lifting the rider for an instant and then putting it back on the beam. The balance may be started swinging by blowing gently on one pan with a device such as a medicine dropper. If the balance is started swinging by fanning with the hand, it should be allowed to make one or two complete oscillations before a reading is taken, to prevent air currents from interfering with the normal swing. Have the amplitude of swing not more than one or two divisions each side of the center.

In reading the position of the pointer on the ivory scale, arrange always to have the reading eye in the same position relative to the ivory scale, that is, in a plane perpendicular to the scale and passing through the center graduation. A mark may be made on the glass door by which to line up the eye before each reading. The final reading must be made with the door closed.

Arrest the swinging of the balance when the pointer is at the center of the scale. This prevents any undue jarring of the beam, which is very likely to get the balance out of adjustment. Always turn the balance out of action before adding weights to the pan or taking them from it. When the balance is not in use, raise the beam from the knife-edges and leave the rider on the beam.

Do not allow the direct rays of the sun to strike the balance and never attempt to do close weighing unless the temperature of the room and balance can be maintained virtually constant.

For ordinary accurate commercial work, the weighing of the gold and silver is done by the "method of equal swings," using the rider for the final weighing. For extreme accuracy, as, for instance, in the calibration of weights, the weighing is done by "deflection," also called the "method of swings."

Weighing by "Equal Swings."—First of all, the balance is adjusted by the star wheel or, preferably, by the adjusting rider, if one is provided, until the needle swings exactly the same distance on each side of the center, reading always in the same order, say, from left to right. For accurate gold weighing it will be necessary to estimate tenths of divisions on the ivory scale.

Put the substance to be weighed on the left-hand pan and add weights to the right-hand pan until their weight is within a fraction of a milligram of the weight of the substance. Apply the weights in a systematic manner, starting with one which is estimated to be too large. If too large, remove it and try the next smaller weight, always working from larger to smaller weights until within 1 mg. of the true weight.

In trying any weight, have the beam off the knife-edges, put the weight in the pan and gently turn the balance key until the pointer inclines slightly to one side or the other. This swing of only one or two divisions should indicate immediately whether the weight on the pan is too much or too little. Again turn the balance out of action before making any change of weight.

When within a fraction of a milligram of the true weight, shift the right hand, or weighing, rider about, until, when the balance is put into action the needle does not move very decidedly in one or the other direction. Then set the beam swinging one or two divisions each side of the center. If it does not swing evenly, arrest the swing, change the position of the rider and try again. Repeat until the needle swings exactly as when adjusted. After one has become familiar with the balance, only two or three trials of the rider will be necessary.

The weight of the substance is found from the sum of the weights on the pan plus the fractional part of a milligram indicated by the position of the rider on the beam.

Weighing by "Method of Swings."—First, determine the point of rest under zero load by noting the position of the pointer at the extreme swing on each side, taking 3, 5 or a greater odd number of consecutive readings. Call the center division zero and count divisions and estimate tenths to each side, calling those to the left of the center −, and to the right +.

Average the readings for each extreme, add the two and divide the sum by 2; the result is the point of rest. The method is illustrated in the following example.

$$\begin{array}{rr@{\qquad\qquad}rr}
 & \text{LEFT} & & \text{RIGHT}\\
 & -\ 3.9 & & 3.6\\
 & -\ 3.7 & & \underline{3.4}\\
 & \underline{-\ 3.5} & 2\,\big| & \underline{7.0}\\
3\,\big| & \underline{-11.1} & & 3.5\\
 & -\ 3.7 & & \\
 & \underline{+\ 3.5} & & \\
2\,\big| & \underline{-\ 0.2} & & \\
 & -\ 0.1 & = \text{point of rest} &
\end{array}$$

Or the point of rest would be 0.1 division to the left of the center.

Call the point of rest under zero load r. Place the object to be weighed on the left-hand pan and weights on the right-hand pan until equilibrium is nearly established. With the rider determine the weight to the next smaller 0.1 mg. Set the beam swinging as before and find the position of rest for the pointer. Call it r'. Shift the rider to the right one whole division (0.1 mg.), so as to bring the point of rest on the opposite side of r, find the position of rest again and call it r''. The fraction of a milligram to be added to the weights and rider reading when r' was found is, then,

$$\frac{r'-r}{r'-r''}\times 0.10.$$

For instance, let the weights and rider reading be 27.4 mg. and let

$$r' = -1.4 \text{ and } r'' = +1.6.$$

Then
$$\frac{r'-r}{r'-r''} = \frac{-1.4+0.1}{-1.4-1.6} = \frac{-1.3}{-3.0} = +0.43$$

and the true weight would be $27.4 + (0.43 \times 0.1) = 27.44$ mg.

Another method of weighing by "deflection," requiring a knowledge of the sensitivity of the balance, is as follows: Suppose that a weight of 0.01 mg. will cause a deflection of the point of rest of 2.0 divisions on the ivory scale. Adjust the balance so that the point of rest with no load corresponds to the zero of the ivory scale. Place the substance to be weighed in the left-hand pan and again determine the point of rest. Suppose the deflection to be 1.2 divisions. Then the weight of the substance is 0.06 mg. With a good balance this is a rapid and accurate method for small amounts of gold, but is not very commonly used.

Weighing by Substitution.—This method of weighing is the one usually adopted for the standardization or adjustment of weights, as it avoids any possibility of error due to inequality of arms. It consists simply in placing the substance to be weighed on one pan, counterbalancing it with weights placed on the other pan and then removing the substance and adding standard weights until the balance is again in equilibrium. The weight of the substance is obtained from the substituted weights.

Sampling.—The sampling of ores of precious metals is a very difficult matter frequently, because of the non-uniform way in which the precious metals are distributed in ores. We will assume for the purpose of present description that the ore brought to the laboratory for assay has been obtained in the proper manner for a representative sample. This ore must be crushed and quartered, taking great care that no flakes of precious metal are lost in the process. The quarter is crushed finer and again quartered and the process repeated until a sample weighing, say, a pound is obtained. This sample should be ground in a ball mill with flint pebbles until it will pass through a 100-mesh sieve (10,000 openings to the square inch). Great care must be taken that no flakes of precious metal remain on the sieve. If there should be any such flakes, they should be put back into the ball mill and the grinding continued until they are reduced to size small enough to pass through the sieve openings. The finely ground sample should then be placed in a quart jar and thoroughly shaken until the mixture is absolutely uniform.

The Crucible Assay.—In order to make an intelligent charge for the crucible assay, it is necessary first to examine the ore to get an approximate idea of the nature of the minerals present. This is done by placing a few grams of the ore (after having been ground) on a vanning plaque or shovel or clock glass. Cover the ore with water, allow to stand until thoroughly wet and agitate until all clumps are broken up, then shake the glass while a current of water is kept running over. The ore will settle in the shape of a fan in the order of the specific gravities of the minerals. The same end may be accomplished more easily by putting the ground ore in a glass tube about ½ in. in diameter, filling with water, then inverting the tube and allowing the minerals to settle. The tube should be about 3 ft. long and the ore should have been ground to 100-mesh size. Examine the strata carefully After a little experience one can readily classify the ore into one of the following classes:

Class 1. Siliceous ore, low in sulfides, arsenides, etc.

Class 2. Reducing ores, high in sulfides, etc. One gram of pyrite will reduce about 11 grams of lead, one of galena about 3.4 grams of lead, one of chalcopyrite about 8 grams of lead and one of sphalerite about 8 grams of lead. These should be further classified according to the nature of the sulfides or arsenides present, such as chalcopyrite, arsenopyrite, etc.

Class 3. Oxidizing ores, high in oxides of iron, manganese and carbonates.

Excess Litharge Charge.—For siliceous ores low in sulfides, weigh 1 assay ton of the finely ground and well-mixed ore on an ordinary analytical balance, transfer to a quart jar, weigh roughly on a pulp balance 40 grams of Na_2CO_3, 10 grams of borax glass and 60 grams of litharge, and if the ore is free from sulfides, add 3 grams of argols. Shake thoroughly in the quart jar until intimate mixture of the ore and flux is obtained, then transfer to a 30-gram (capacity 225 c.c.) Denver fire-clay crucible. If the ore contains copper, it is well to increase the PbO to 100 grams, but this increases silver loss slightly.

For clayey ores modify the above charge by increasing the amount of borax glass to 12 grams, and if the ore is extremely clayey, add also 5 grams of sodium fluoride.

For reducing ores of class 2, account must be taken of the amount of litharge which will be reduced by the sulfides. The argols generally used will reduce about 9 grams of lead per gram of argols. Since sulfides also reduce lead, the amount of argols used must be reduced according to the amount of sulfides present. If the amount of sulfides present is so great as to make a lead button greater than 25 grams in weight, some KNO_3 should be added to decrease the reducing power of the ore. One gram of KNO_3 will oxidize about 4 grams of lead. If the amount of sulfides is so great as to require more than 10 or 12 grams of niter, the ore should be assayed either by the soda-iron method given below, or it should be roasted and assayed by the following charge:

Oxidized ores are assayed by the same charge as given for siliceous ores except that more argols are required and about 10 grams of silica should be added.

In case the ore is so high in sulfides that it is best to roast it, weigh 1 assay ton of the ore and transfer to a 5 in. scorifying dish, put in a muffle and heat to a dull red. After the sulfur seems to have burned off, raise the temperature to about 700°C. and cautiously stir occasionally. Treat the ore then as directed for oxidizing ores.

Soda-iron Charge.—In this charge the amount of litharge used cannot be greater than 30 grams, since all of the lead oxide is reduced by the iron. In this method, instead of depending upon the oxidizing power of litharge to decompose the sulfide minerals which might contain precious metals, iron is relied upon as indicated on page 397. The sulfide of iron resulting should dissolve in the slag. Use the following charge: One assay ton of ore, 65 grams of Na_2CO_3, 30 grams of litharge, 15 grams of borax glass and 5 grams of silica or powdered glass and three 20-penny nails. The slag obtained from the soda-iron method contains sodium and iron sulfide and has a slight solvent power for silver, hence the results for silver are apt to be low but the gold is not affected. The method is not good for ores containing much nickel, copper, cobalt, arsenic, antimony, bismuth or tellurium.

Fusion.—Whatever charge is used, cover the charge in the crucible with about $\frac{1}{8}$ in. of salt, put in a muffle or pot furnace and *gradually* raise the temperature until the contents of the crucible are in a state of quiet fusion. Keep the contents of the crucible molten at the lowest temperature at which it is entirely liquid, for 10 minutes, raise the temperature somewhat and pour into a conical iron mold. When the contents of the mold are cold, remove and knock the slag off the lead button. Break up the slag and observe if any particles of lead remain in it.

Save the slag. If the lead button weighs between 20 and 30 grams, it is ready for cupellation. If the lead button is small, it is probable that not all of the precious metals have been gathered in it. In this case the fusion should be repeated, using a fresh sample with a larger amount of argols. If the lead button is abnormally large it should be reduced in size by partial cupellation, the cupel cooled and cupellation finished with a new cupel. The abnormally large lead button indicates that the charge in the crucible should have contained less argols or more niter.

In the case of the iron nails method, just before pouring, the nails should be removed by a pair of tongs, taking care that all lead adhering to the nails is shaken off into the crucible.

Cupellation.—Prepare cupels by gradually pushing 1½-in. Denver Fire Clay Company's "Casite" cupels or homemade bone ash cupels into a muffle heated to 950°C. at the hottest part of the muffle at the back. When fully heated, draw the cupels to the front of the muffle and drop the lead buttons into the cupels, taking care that the position of the cupels is noted so that the identity of the precious metals obtained from cupellation may not be lost. The cupels should be numbered. As soon as the lead has been put in the cupels, push them back to the hotter part of the muffle. As soon as the lead is melted and commences to oxidize, rapidly draw the cupels toward the front of the furnace where the temperature is about 820°C. and where litharge feathers form near the top of the cupel on the side toward the front of the furnace. Continue the cupellation at this temperature until the button left commences to assume a rounded form, when the cupel should be pushed back gradually toward the hotter part of the furnace. As the last of the lead disappears the button suddenly freezes, with liberation of its latent heat and with a momentary brightening. Leave the cupel in the furnace for about one minute after the brightening, draw the cupel to the front of the furnace and allow to stay several minutes, then remove entirely from the furnace and allow to cool.

When the bead is cold, detach it from the cupel with a pair of pliers and brush with a stiff brush to remove bone-ash. When free from bone-ash, weigh carefully as described on page 401.

Parting.—Put the bead of precious metals in a small porcelain crucible and add several cubic centimeters of 1:7 HNO_3 (sp. gr.

1.06). Put on the hot plate and heat nearly to boiling. The bead should dissolve with evolution of bubbles. If bubbles do not come off at once, add HNO_3, a few drops at a time, until action starts. If the bead contains more than four parts of silver to one of gold, no trouble will be experienced in the parting. If the gold is too high in amount in proportion to silver, difficulty will be encountered. In this case, it is best to place the bead in a cupel with a few grams of lead and a carefully weighed amount of pure silver sufficient to raise the proportion of silver to gold above 4:1, finish the cupellation and again part. Continue the heating until the acid has dissolved the silver and action ceases. Pipette off the solution, taking care not to withdraw any of the gold residue in the bottom of the crucible, then add a few cubic centimeters of 1:1 HNO_3 and heat nearly to boiling for several minutes. Pipette off this solution and wash several times with distilled water, pipetting as completely as possible each time. After all the silver has been washed out, remove the few drops of water remaining in the crucible with a small piece of filter paper, taking care that no gold adheres to the filter paper. Finally, set the crucible on a hot plate to dry, avoiding spattering, and finally anneal the gold over a burner at a bright red when the gold will turn from its dark amorphous appearance to the bright yellow of pure gold. Transfer this to the balance pan and weigh extremely carefully. The amount of silver in the ore is obtained by subtracting the weight of the gold from the weight of the silver plus gold, making correction for any silver added.

Notes.—It is sometimes desirable to make a preliminary assay of the ore to determine the amount of argols or niter which may be required for the regular assay. An experienced assayer, however, can judge this with sufficient accuracy by "panning" the ore. An examination of the slag of this preliminary run will show whether the charge used was correct or not.

The ore and fluxing materials, especially the litharge, should be very intimately mixed, since each particle of the gold should come into contact with the droplet of lead to carry it to the bottom. Slow fusion of the charge also helps.

The charge should not fill the crucible more than two-thirds full, since if too full the charge may froth over, especially if niter is used.

When the charge is poured from the crucible into the iron mold, it should pour clean and with no tendency for particles of lead to stick to the crucible or to remain suspended in the slag.

An excessive amount of litharge should not be used, because it tends to make silver dissolve somewhat in the slag.

When the lead button is put into the hot cupel, it is quickly covered with a black scum, which should disappear when the temperature has reached about 850°C. If the oxide scum does not disappear promptly and the lead oxidation "drive" rapidly, the temperature is probably too low. If there is great delay in this driving, a loss in silver usually results.

Any foreign elements, like copper, arsenic, zinc, are oxidized during the cupellation and absorbed in the cupel or volatilized when not present in too large amounts.

The sodium and lead silicates formed by the above charges with a siliceous ore are easily fusible and easily dissolve other basic oxides such as FeO, Al_2O_3, MgO, CaO, etc., when in moderate amounts. But highly basic ores require the addition of considerable silica to form a sufficient amount of sodium silicate to dissolve the basic oxides present.

When a large number of cupellations are being carried on in a muffle, instead of varying the temperature by pushing the cupel about, the temperature of the muffle itself is regulated by regulating the gas and draft.

After the cupellation is finished, the cupel should not be allowed to remain in the hot part of the muffle more than one minute, owing to loss of silver by volatilization.

When the finishing temperature is too low, the beads will solidify without brightening and retain lead and have a dull appearance.

When the bead is high in gold a higher finishing temperature is required.

If the upper surface of the bead appears to be frosted, the presence of tellurium or members of the platinum group is indicated. When a large amount of platinum is present, the bead flattens and will not brighten.

If the ore contains much antimony, some will be in the lead button and shows as yellow scoria around the cupel, which solidifies as soon as formed and expands and breaks the cupel. Arsenic behaves similarly.

Bismuth is less readily oxidized than lead and tends to remain in the silver. It causes a ring of orange yellow around the silver bead.

Copper is less readily oxidized than lead. Its oxide dissolves readily in molten litharge, going into the cupel with it and staining the cupel a dirty green. It tends to contaminate the silver button.

Tellurium gives the surface of the cupel a pinkish color, which fades on cooling. It causes loss of precious metal and also, since it is not readily oxidized, it tends to contaminate the bead.

As little as 1.6 per cent of platinum gives a characteristic frosted appearance to the silver bead which is visible to the naked eye, while lower amounts may be apparent by the use of a microscope.' Palladium does the same. As little as 0.004 per cent of rhodium causes a distinct crystallization visible to the naked eye. The presence of 0.03 per cent rhodium always causes the silver bead to spit.

All beads containing much silver should be withdrawn from the muffle slowly or they will sprout and spit with loss of silver, owing to the liberation of gas upon solidification.

When it is suspected that the amount of silver in the ore will be insufficient to result in a ratio of 3 or 4 of silver to 1 of gold, it is well to add a carefully weighed amount of silver to the cupel.

The bead on parting with nitric acid should give an adherent residue of gold. However, the gold often breaks up into a fine powder and great care must be taken that none of this is lost in decantation.

Scorification Assay.—This is the simplest method and consists simply of an oxidizing fusion of the ore with lead and borax glass in a scorification dish. The lead oxide formed combines with silica and other materials of the ore, forming a fusible slag. The scorifying dish is a shallow fire-clay dish 2 to 3 in. in diameter. The amount of ore used is from 0.10 to 0.25 A.T. With this is used about 50 grams of test lead and a few grams of borax glass. Since such small samples must be used, this method is only applicable to rich materials like concentrates and bullion.

Process.—Carefully weigh 0.10 to 0.20 assay ton of the thoroughly mixed sample, transfer to the scorifying dish, which should already contain 25 grams of test lead, mix the lead and ore and add 25 grams more of the test lead with 1 gram of borax glass. Put the scorifier (which should have been previously warmed) into a muffle at a full red-heat and close the door until the lead is melted. As soon as fusion is complete, open the door partially to allow a current of air to pass through the muffle. At this stage some of the ore may be seen to be floating on the surface of the molten lead, and any sulfides present are rapidly oxidized, chiefly by the air, but partly by the litharge which immediately begins to form. The sulfur, arsenic, antimony, etc. in sulfides and arsenides are thus soon eliminated as volatile oxides, while the base metals are converted into oxide, and combine with the litharge and borax to form a fusible slag. Silica also forms a fusible compound with the litharge. Thus the litharge, as fast as it is produced, reacts on the various substances contained in the ore, forming with them a clean slag, while the previous metals pass into the unoxidized lead into the bottom of the scorifier.

The slag as it is produced forms a ring, leaving the center of the lead bath or "eye," as it is termed, exposed to oxidation. As oxidation of the lead continues, the litharge flows to the sides and increases the quantity of slag, until at length the whole of the lead is covered with slag and the eye has disappeared, leaving a flat, uniform surface. The scorification is then considered finished, but it is usual, before pouring, to clean the slag. This is done by placing a pinch of charcoal or coal powder (about 0.2 gram), wrapped in tissue paper, on the surface of the slag, with a pair of tongs, and closing the muffle door. A small quantity of litharge is thus reduced, forming a number of globules of lead which sink in the slag, alloying with any silver and gold which the slag may contain, and concentrating them in the molten lead below. The temperature at the finish should be sufficiently high to liquefy the slag completely. A temperature of 1,050 to 1,100° C. is usually enough. When the slag has again become tranquil, the scorifier is withdrawn, and the contents poured into an iron mold. The contents should pour clean and not leave any imperfectly fused material attached to the surface of the scorifier. The assay should be poured as soon as finished, and not left in the muffle, as oxidation of the lead will continue, although none is exposed to the air, owing to the interchange of oxygen between litharge and other oxides present. When cold, the slag is detached from the button of lead as already described. The lead button should be comparatively soft and malleable, and weigh from 15 to 20 grams. In most cases the button may be cupelled direct, but if it weighs much more than 20 grams, its weight is reduced by another scorification.

Notes.—The size of scorifier to be used depends upon the amount of ore, lead, borax glass and silica used, and should be such as to give a button of approximately 15 to 18 grams. If a large scorifier is used with a small amount of lead, the resulting lead button will be very small and a high loss of silver will result. Again, the larger the amount of borax glass used the more slag there will be and the sooner the lead will be covered.

If the ore contains much tin, antimony, arsenic, nickel or large amounts of basic oxides, such as hematite, magnetite, etc., an infusible scoria is almost certain to form on the surface of the slag or on the sides of the scorifier which neither a high temperature nor extra borax glass will remove. As this scoria is likely to enclose particles of undecomposed ore, the only safe procedure is to make a fresh assay with less ore, and with such other changes in charge and manipulation as the experience of the first assay may suggest.

Litharge, being a strong base, has a great affinity for the silica of the scorifier and, especially, when mixed with copper oxide, it attacks this silica readily. When scorifying matte and copper bullion it is often necessary to add powdered silica to the charge to prevent a hole being eaten through the scorifier.

Hard buttons may be due to copper, antimony or, in fact, almost any metal alloyed with the lead. Brittle buttons may be due to one of many alloyed metals, or to the presence of sulfur or lead oxide.

The scorification assay is simple, inexpensive and reasonably rapid. For the determination of silver in sulfide ores having an acid gangue, it is generally satisfactory and widely used. It is particularly suited for the determination of silver in ores containing considerable amounts of the sulfides, arsenides or antimonides of the difficultly oxidizable base metals.

Blanks and Corrected Assay.—The litharge and test lead used in fire assay almost always contain traces of silver. To determine the amount, make up a charge just as if an ore were to be analyzed, except that about 20 grams of pure silica are used instead of ore, and carry out the regular procedure for fire assaying. The gold and silver found will be the blank which should be subtracted from the regular results. However, there are numerous losses which must be corrected for. These losses include volatilization losses and slag losses. The best method of determining these is to make up another charge as directed for the blank determination and add very carefully weighed amounts of pure gold and pure silver about equal to the amount found in the uncorrected assay. Add these weighed amounts of gold and silver to the charge and carry through the assay as usual. After making correction for the blank determination, the amount of gold and silver lost is calculated and corrections made on the results of the regular assay.

Instead of adding known amounts of gold and silver, the slag obtained in the crucible assay and the contaminated part of the cupel may be ground together and assayed, adding a sufficient amount of litharge and reducing agent and flux to get a proper sized button and a fluid slag. The gold and silver thus recovered are added to the results obtained in the regular assay. The results corrected in this way are apt to be high because of the fact that the gold-silver beads are always somewhat impure.

Assay of Lead Bullion.—Lead bullion is assayed exactly as directed for the cupellation process. It is necessary, in case of rich material particularly, to make a check assay on a known amount of gold and silver in order to make corrections for cupellation losses.

Copper bullion is assayed either by the scorification process or by combination of wet methods and fire assay. When the scorification assay is used, 0.25 A.T. samples of the finely mixed drillings are mixed in 3-in. scorifiers with 50 grams of test lead, covered with 40 grams more and 1 gram of SiO_2 is added. Scorify as usual, pour and rescorify with 60 grams of test lead and 1 gram of silica. Carry out the above on four different samples. Combine the buttons so that there will now be two samples, add 85 grams of test lead and 1 gram of SiO_2, scorify very cool, again add 70 grams of test lead and 1 gram of SiO_2 and scorify for the fifth time. Cupel the button as usual. Results for gold are excellent, but those for silver are low, running as much as 5 or 10 per cent low.

The Detection and Estimation of Platinum.—The method as given below is as found in *Technical Paper* 270, U. S. Bureau of Mines by C. W. Davis.

The bead obtained by usual fire-assay methods may contain gold, silver and the platinum metals and is parted with HNO_3. The silver and most of the platinum and palladium go into solution. The residue may contain gold, iridium, rhodium and some ruthenium and osmium, as well as platinum. The gold and the rest of the platinum are dissolved from the residue of other platinum metals with dilute aqua regia and filtered off, leaving iridium, rhodium, part of the ruthenium and a small amount of osmium, which may be ignited and weighed. The HNO_3 solution may contain silver, platinum and palladium. The silver is removed, as the chloride and the platinum and palladium are precipitated from the solution (which has been made slightly alkaline with Na_2CO_3), by boiling with formic acid, then filtered, ignited and weighed. To separate the palladium from the platinum, the mixed metals are treated with warm dilute HNO_3, which dissolves the palladium and leaves the platinum. The palladium is found by difference, or may be precipitated with formic acid, after evaporating to dryness with HCl, taking up with water, and neutralizing with Na_2CO_3. The aqua regia solution is evaporated to dryness twice with HCl, taken up with water, and, after the gold is removed with oxalic acid, the platinum and palladium are recovered as in the preceding process. A qualitative test is applied to a solution of the platinum precipitate.

Procedure.—The ore in all cases is ground to pass a 100-mesh screen and when substances difficult to fuse, such as chromite and zircon, are present, the sample should be made to pass a 150-mesh screen.

When the quantity of platinum is small, it is advisable to run several samples of an assay ton each, combine the lead buttons, and scorify to about 30 grams.

An assay ton of the carefully sampled ore is thoroughly mixed with a suitable flux. As iron has a greater affinity for iridium than has lead, the old iron-nail method of treating sulfide ores should not be used.

If there is not at least 15 times as much silver as platinum in the ore, enough of a silver salt—chloride or nitrate—is added to make up the deficiency. The presence of excess silver is required to render the platinum soluble in HNO_3 when parting, to assist in removing the last traces of lead in cupelling and to lessen any tendency toward loss in the cupel. The addition of silver in the form of a salt makes possible a thorough mixing with the charge, and, when reduced, the numerous silver particles are distributed in a way to be most effective in collecting the platinum.

To an unknown ore, about 0.05 gram of silver chloride may be added. The charge is fluxed as in the ordinary fire assay for gold and silver, except that after the fusion has become quiet the temperature should be raised somewhat higher than is the usual practice and the heating continued for about an hour. The crucible is removed from the furnace without agitating the contents and left to cool. Cooling without agitation prevents loss of iridium, ruthenium and osmiridium, which do not alloy with lead but sink through it and are held mechanically when the button cools. If the charge is poured, these metals are apt to be partly lost.

The button is freed from slag and cupelled at a high temperature. As the high temperature causes a loss of silver, a check or proof assay should be run at the same time to be used in correcting this error.

When platinum makes up over 1.6 per cent of the bead, the latter appears frosted to the unaided eye. The microscope will detect platinum when it constitutes 0.3 per cent of the silver bead. Considerable quantities of platinum make the bead flat and irregular. The roughness caused by iridium is of finer texture than that due to platinum. Palladium gives the surface of the bead an embossed appearance. Ruthenium in quantity turns the surface to a bluish-black color, a black scum being left on the cupel. After cupeling, the button is then parted with HNO_3, first with 1:4, then with 1:1, and finally with 2:1 acid. If gold, silver and all the platinum metals are present in the ore, the silver, palladium and platinum are dissolved by this treatment, leaving the gold, iridium, rhodium and some ruthenium and osmium. Most of the osmium and part of the ruthenium are oxidized and lost during cupellation. Part of the iridium may not collect in the silver and will be lost on the cupel.

If considerable platinum is found, some will be left still undissolved. The residue is filtered off on a 5-cm., ashless filter paper, washed with dilute HNO_3 (pure water causes the colloidal metal to pass through the paper), ignited and saved for the recovery of any residual platinum as well as for the determination of iridium and rhodium.

Dilute HCl is then added to the filtrate slowly, with constant stirring to precipitate the silver. After this has set overnight, the silver chloride is filtered off and washed with water, acidulated with HNO_3. If the precipitate is pink, it must be redissolved and again precipitated to remove occluded platinum or palladium. Although palladium may be separated from silver by one precipitation as the chloride, in acetic acid solution, the addition of the ammonia necessary to neutralize the HNO_3 present causes a bulk of salts on evaporation, which interfere with the subsequent operations.

Evaporate the filtrate just to dryness, do not bake; take up with dilute HCl and again evaporate just to dryness, then take up with dilute HCl, transfer to a 30-c.c. beaker and evaporate nearly to dryness (until there is a dry spot in the center of the beaker). When cold, take up with a very little cold water and filter on a 5-cm. paper to remove the last traces of silver. It is important that all the silver be removed at this point, otherwise silver would come down on boiling with formic acid and vitiate the platinum-palladium result.

The filtrate is made slightly alkaline with Na_2CO_3, formic acid added and the solution boiled in a covered beaker until all the platinum and palladium are precipitated (about 30 minutes). These finely divided metals are filtered on a small (5-cm. or less) paper, washed with hot water, ignited and weighed. As the platinum metals adhere to both glazed and unglazed porcelain crucibles on ignition, "impervite" crucibles may be used to advantage for the ignition of the finely divided metals. In transferring the platinum metals from the beaker to the filter, it has been found convenient to use a small wash bottle which will deliver a very fine stream of water. Funnels that have been cut down so that the small filter papers extend beyond the rim prevent the fine metals from creeping.

The filtrate should be boiled again with formic acid to confirm a complete precipitation of the platinum metals.

If the first parting solution is yellow or orange, the presence of palladium is indicated and the platinum may be separated from the palladium and determined. Warm the metals with dilute HNO_3 (1:4), which quickly and completely dissolves the palladium, filter, wash, ignite and weigh the pure platinum. The palladium may be found by difference, or it may be precipitated by formic acid from the solution obtained by evaporating to dryness with HCl, dissolving in water and neutralizing with Na_2CO_3.

The residue from HNO_3 parting (which may contain gold, iridium and rhodium, as well as some ruthenium, osmium and undissolved platinum) is treated with 1:5 aqua regia, dissolving the gold and platinum. The residual platinum metals are filtered off on a small filter paper, ignited (using "impervite" crucibles) and weighed. The aqua regia solution, which may contain gold and platinum, is evaporated to dryness, taken up with HCl and again evaporated to dryness, then extracted a second time with HCl, evaporated nearly to dryness, taken up with cold water and any residual matter is filtered off. The solution is then boiled with oxalic acid until the gold is all precipitated. It is well to let the solution stand overnight before filtering off the gold. The gold is filtered off and the platinum, recovered by boiling the solution which has first been neutralized with sodium carbonate with formic acid, is then filtered off, ignited and its weight added to that of the platinum already found.

It is advisable to check results by running a known sample along with the unknown. This known sample is made by adding to a crucible charge the approximate quantity of gold, silver and the platinum found in the ore. The check is treated in every way the same as the sample to be examined, the latter being corrected if the known sample shows a discrepancy.

The resulting platinum and palladium should be dissolved separately in aqua regia, taken to dryness twice with HCl, extracted with water, and, after each solution has been acidified with HCl, tested qualitatively, KI giving a red color with platinum and a dark brown precipitate with palladium.

REFERENCES ON ASSAYING:

FULTON, "A Manual of Fire Assaying."
BUGBEE, "Textbook of Fire Assaying."
LODGE, "Notes on Assaying."
SMITH, "The Sampling and Assay of the Precious Metals."
SEAMON, "Manual for Assayers and Chemists."
BERINGER, "A Textbook of Assaying."
PARK, "A Textbook of Practical Assaying."
RICKETTS and MILLER, "Notes on Assaying."

CHAPTER XLV

WATER ANALYSIS

The processes of analysis of water as given in this book are for waters which are to be used for industrial purposes, such as boiler purposes, cooling water for blast furnace boshes and similar purposes, where the formation of scale or corrosion is a matter of concern. Some of the methods of sanitary analysis are added, but the complete examination of water for sanitary purposes or drinking water is out of the scope of this book.

The scale-forming materials in water are $CaH_2(CO_3)_2$, $MgH_2(CO_3)_2$, $CaSO_4$, $MgSO_4$, $CaCl_2$, $MgCl_2$, $Fe_2(SO_4)_3$, SiO_2, $Al_2(SO_4)_3$ and other salts. The most common compounds which give trouble in boilers by causing scale are the first four given above, except in the case of mine water, when sulfates of iron and aluminium are frequently present.

Water is softened by adding lime (CaO) and soda ash (Na_2CO_3). The reactions are:

$$CaH_2(CO_3)_2+CaO=2CaCO_3+H_2O.$$
$$MgH_2(CO_3)_2+2CaO=Mg(OH)_2+2CaCO_3.$$
$$MgSO_4+CaO+H_2O=CaSO_4+Mg(OH)_2.$$
$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

DETERMINATION OF SILICA, IRON OXIDE, ALUMINA, LIME, MAGNESIA AND ALKALIES

Silica.—Acidify 1,000 c.c. of the water with 10 c.c. of strong hydrochloric acid, and evaporate to dryness in a platinum or porcelain dish. Heat the dish for an hour longer in the air-bath at a temperature of about 125°C. Moisten the residue with 10 c.c. of strong hydrochloric acid, heat for a few minutes, then add about 30 c.c. of water, heat to boiling and filter into a No. 2 beaker. Clean the dish thoroughly, and wash the filter free from chlorides, reserving the filtrate for determining other mineral constituents. Ignite the residue with the filter, and weigh as SiO_2. Moisten the residue in the crucible with 1 drop of sulfuric acid, then add a little hydrofluoric acid, and evaporate to dryness. If there is a residue, ignite and weigh, making the correction for the silica, dissolve the residue by digestion with strong hydrochloric acid and add the solution to the main portion.

Iron and Aluminium Oxides.—To the filtrate from the silica add ammonia in slight excess, heat to boiling and filter into a No. 3 beaker. Wash the residue free from chlorides, ignite and weigh as Fe_2O_3 and Al_2O_3. To determine the iron oxide and alumina separately, proceed as follows: Dissolve the iron from the residue by digestion with strong hydrochloric acid, add 1 c.c. of strong sulfuric acid and evaporate until the white fumes are obtained. Dissolve the ferric sulfate with water, transfer to a 50 c.c. flask and titrate the iron as directed on page 380. Calculate to Fe_2O_3 and determine the alumina by difference.

Lime.—To the filtrate from the iron and aluminium hydroxides add 20 c.c. of strong ammonia and 15 c.c. of ammonium oxalate solution, heat and, if necessary, concentrate until the calcium is completely precipitated. Filter into an evaporating dish, wash the filter free from chlorides, ignite and weigh as CaO. Concentrate the filtrate to about 150 c.c., transfer to a 200-c.c. flask with graduation mark and, when cool, make up to the mark and mix.

Magnesia.—With a pipette transfer 100 c.c. of the solution in the 200-c.c. flask to a No. 3 beaker, rinsing the adhering liquid in the pipette back into the flask. Add to the solution slowly, and with rapid stirring, 10 c.c. of ammonium sodium hydrogen phosphate solution, then add 25 c.c. of strong ammonia, and let stand for 12 hours. Filter off the precipitate, wash it free from chlorides with ammonia (1:4), ignite at a low temperature and weigh as $Mg_2P_2O_7$.

Alkalies.—Transfer the rest of the solution from the 200-c.c. graduated flask to a No. 3 beaker, add a slight excess of ammonia, then some milk of lime and boil to precipitate the magnesia. Filter, precipitate the calcium in the filtrate by boiling with a little ammonium oxalate, and filter into a platinum or porcelain dish. Evaporate the solution to dryness, and ignite to volatilize the ammonium salts. Heat all parts of the dish finally to dull redness, but do not raise the temperature above that necessary to expel volatile matter. Take up the residue with water, make slightly ammoniacal and add a few drops of ammonium oxalate solution to precipitate any calcium that may remain. Filter into a small, weighed dish, and again evaporate to dryness and ignite to expel ammonium oxalate. Weigh the residue as NaCl and KCl. If pure, it will be perfectly soluble in water.

If the alkalies are to be determined separately, take up the residue of chlorides with water and a few drops of hydrochloric acid, then add an excess of platinic chloride solution and evaporate to pastiness on the water-bath. Take up the residue with 80 per cent alcohol and filter, washing the residue thoroughly with the alcohol. The sodium salt is dissolved, and the potassium salt remains insoluble in alcohol, but is freely soluble in water. Place under the filter a small, weighed dish, and dissolve the potassium salt on the filter with hot water. Evaporate the solution on the water-bath; dry for half an hour at 100°C., and weigh as K_2PtCl_6. The sodium may then be found by difference.

DETERMINATION OF TOTAL DISSOLVED MATTER AND SULFATE

Put 500 c.c. of the water in a weighed platinum or silica dish, and evaporate to dryness on the water-bath. Dry the residue in the air-bath at 105°C. to constant weight. Weigh the residue as total dissolved matter. If the water carries suspended matter, it should be filtered.

Treat the above residue with 5 c.c. of strong hydrochloric acid, add about 50 c.c. of water; boil for a few minutes and filter into a No. 2 beaker. After adding the washings of the residue, heat the filtrate to boiling and add 5 c.c. of a 20 per cent solution of barium chloride. Allow to stand in a warm place until the precipitate settles readily, filter, wash free from chlorides and ignite at low temperature in an open crucible. Weigh as $BaSO_4$.

Total Solids and Ignition Loss.—First, evaporate 100 c.c. of the clear water (filtered if necessary) to dryness in a weighed platinum dish, and dry at 100° to constant weight. This gives the "total solids." After weighing the dish, ignite it very cautiously, not passing a barely visible red-heat, until the residue becomes nearly white. Weigh again after cooling in a desiccator. The loss is water of combination and organic matter, and the residue is the fixed mineral matter.

Suspended Matter.—Prepare a dilute cream of asbestos fiber which has been finely shredded, thoroughly ignited, treated with strong hydrochloric acid for at least 12 hours and washed with distilled water until free from acid.

Procedure.—Prepare a mat of the asbestos fiber $\frac{1}{16}$ in. thick in a Gooch crucible. Dry it in an oven at 103°C., cool and weigh. Filter 1,000 c.c. of the sample or sufficient water to obtain 50 to 100 mg. of suspended matter. Dry for one hour at 103°C., cool and weigh. Report the temperature at which the residue was dried. If 1,000 c.c. are filtered, the increase in weight expressed in milligrams is equal to parts per million of suspended matter.

HARDNESS

A water containing certain mineral constituents in solution, chiefly calcium and magnesium, which form insoluble compounds with soap, is said to be hard. Carbon dioxide in water increases the solubility of calcium and magnesium carbonates, forming bicarbonate. If carbon dioxide is removed from the water by boiling, the bicarbonate is decomposed and calcium and magnesium are partly precipitated. The proportion of calcium or magnesium carbonate that a water can hold in solution depends on the concentration of carbon dioxide, which, in turn, depends on the temperature of the water and the proportion of carbon dioxide in the atmosphere with which the water has been in contact. Consequently, when the carbon dioxide is removed from the water by boiling or otherwise, the carbonates of calcium and magnesium are partly, but not completely, precipitated, and the hardness of the water is thus diminished and the water is softened to the extent to which these substances are removed. The hardness removed by boiling is called "temporary hardness."

DETERMINATION OF HARDNESS

(Soap Test)

Standard Solutions.—Dissolve 13 grams of pure castile soap, or, better, 13 grams of sodium oleate, with a mixture of 500 c.c. of alcohol and 500 c.c. of water; let stand overnight, and filter if it is not clear. To standardize this solution, take 1 gram of pure calcium carbonate in a porcelain dish, dissolve with dilute hydrochloric acid, added in slight excess, and evaporate on the water-bath. Dissolve the residue with water, and again evaporate to dryness to expel the hydrochloric acid. Dissolve the calcium chloride with water, and make up the volume to 1 liter. Measure from a burette 12 c.c. of this solution into a wide bottle or flask of about 200-c.c. capacity; make up the solution to 100 c.c. with recently boiled distilled water, and then from a burette add the soap solution in small portions at a time until, after shaking, a lather is formed which remains unbroken for three minutes. Dilute the soap solution as necessary so that exactly 12 c.c. will be required when 12 c.c. of the standard calcium chloride are taken.

Total Hardness.—Take 100 c.c. of the water, shake well, suck the air from the flask to remove carbon dioxide and titrate as above until the persistent lather is obtained. The number of cubic centimeters used, multiplied by 10, gives the total hardness in parts per 1,000. Add about 1 c.c. of the soap solution before each shaking and less toward the end of the titration.

If more than 14 c.c. of the soap solution are required with 100 c.c. of the water, take 50 c.c., and if 14 c.c. of the standard are still insufficient, take 25 c.c. of the water, diluting the sample in any case to 100 c.c. with recently boiled distilled water.

Greater care is to be exercised with water containing much magnesium carbonate, since the soap does not react so readily with magnesium salts. An apparently permanent lather may form which will break upon standing for a short time.

Permanent Hardness.—Measure 250 c.c. of the water into a flask of 500 c.c. capacity, and boil gently for half and hour, maintaining the volume with frequent additions of recently boiled distilled water. Cool the water quickly, filter, pour it back into the flask, and make up to the mark. Take a portion of 50 or 100 c.c., according to the hardness of the water, and titrate in the same manner as above.

Temporary Hardness.—To find the temporary hardness of the water subtract the permanent hardness from the total hardness. It is the hardness that is removed by boiling.

The hardness of water is due to the presence of calcium and magnesium salts, the carbonates causing temporary hardness. Upon boiling, the lime and magnesia are precipitated, owing to the expulsion of carbonic acid gas from the water. The permanent hardness is due principally to calcium sulfate. It may also be due in part to magnesium sulfate or to the chlorides of lime and magnesium, which salts are not precipitated at boiling temperature.

DETERMINATION OF ACIDITY OR ALKALINITY

Standard Solutions.—Prepare a fifth normal solution of sulfuric acid by adding 6 c.c. of strong sulfuric acid to a liter of water, and after cooling to the surrounding temperature, determining the strength and diluting until 1 liter contains exactly 9.8 grams of sulfuric acid. To determine the strength of the solution, measure from a burette 15 c.c. into a No. 3 beaker, dilute to about 150 c.c., add a few drops of hydrochloric acid, heat to boiling and add 5 c.c. of a 20 per cent solution of barium chloride. Allow to stand in a warm place until the precipitate settles readily when stirred; filter and ignite on a weighed Gooch crucible, or filter on a paper pulp filter and ignite, using the necessary precautions to prevent reduction of the barium sulfate. From the weight of $BaSO_4$ found calculate the H_2SO_4. The acid may also be standardized as directed on page 61.

To 250 c.c. of the water in a No. 4 beaker add 5 c.c. of fifth normal sulfuric acid; heat to boiling, cool and add 3 drops of methyl orange indicator. If the water is shown to be alkaline, titrate with the acid until the neutral point is reached. If the water is acid or does not contain enough alkali to neutralize the acid added, run in the tenth normal sodium carbonate solution from a burette until the neutral point is reached. The acidity is reported in terms of sulfuric acid and the alkalinity in terms of sodium carbonate.

The ratio of the acid to the alkali in the reaction being 49:53, the acidity in parts per 1,000 is found by multiplying the number of cubic centimeters of tenth normal sodium carbonate used, less twice the number of cubic centimeters of acid used, by 0.0196, and the alkalinity is found by multiplying the total number of cubic centimeters of acid used, less half the number of cubic centimeters of alkali required, by 0.0424.

CHLORIDE

Reagents.—1. Standard sodium chloride solution. Dissolve 16.48 grams of pure sodium chloride in 1 liter of distilled water.

Dilute 100 c.c. of this stock solution to 1 liter in order to obtain a standard solution, each cubic centimeter of which contains 0.001 gram of chloride.

2. Standard silver nitrate solution. Dissolve about 2.40 grams of silver nitrate crystals in 1 liter of distilled water. Standardize this with the standard sodium chloride solution, and adjust, correcting for volume so that 1 c.c. will be exactly equivalent to 0.0005 gram of chloride.

3. Potassium chromate indicator. Dissolve 50 grams of neutral potassium chromate in a little distilled water. Add enough silver nitrate to produce a slight red precipitate. Filter and dilute the filtrate to 1 liter with distilled water.

Procedure.—Add 1 c.c. of potassium chromate indicator to 50 c.c. of the sample in a 6-in. white porcelain evaporating dish or a 150-c.c. Erlenmeyer flask over a white surface. Titrate with the silver nitrate solution under similar conditions of volume, light and temperature as were used in standardizing the silver nitrate until a faint reddish coloration is perceptible. The detection of the end point is facilitated by comparison of the contents of the porcelain dish with those of another dish containing the same quantity of potassium chromate indicator in 50 c.c. of distilled water. Some analysts prefer to make the titration in a dark room provided with a yellow light. The end point is very sharp by electric light and also by daylight with photographic yellow glass.

NON-CARBONATE HARDNESS BY SODA REAGENT METHOD

The use of soda reagent does not avoid entirely the error due to solubility of the salts of calcium and magnesium; consequently, if much depends on the results, as in water softening, gravimetric determinations of the calcium and magnesium that remain in solution should be made and a correction should be applied for those amounts.

Reagent.—Prepare soda reagent from equal parts of sodium hydroxide and sodium carbonate. It should be approximately tenth normal.

Procedure.—Measure 200 c.c. of the sample and 200 c.c. of distilled water into 500-c.c. Erlenmeyer flasks. Treat the contents of each flask in the following manner: Boil 15 minutes to expel free carbon dioxide. Add 25 c.c. of soda reagent. Boil 10 minutes, cool, rinse into 200-c.c. graduated flasks and dilute to 200 c.c. with boiled distilled water. Filter, rejecting the first 50 c.c. and titrate 50 c.c. of each filtrate with 0.02N sulfuric acid in the presence of methyl orange indicator. The non-carbonate hardness in parts per million of calcium carbonate is equal to 20 times the difference between the number of cubic centimeters of sulfuric acid required for the soda reagent in distilled water and the number of cubic centimeters of 0.02N sulfuric acid required for the soda reagent in the sample.

Water naturally containing bicarbonate and carbonate in excess of calcium and magnesium requires a larger amount of acid to neutralize the sample after it has been treated than is required to neutralize the volume of soda reagent originally added.

DETERMINATION OF FREE AND ALBUMINOID AMMONIA

Apparatus and Reagents.—A special still is needed for preparing ammonia-free water and for distilling ammonia from water in the process of analysis. This may conveniently be made by connecting a large glass retort, provided with a ground glass stopper, with an ordinary glass tube condenser. The retort tube may be drawn out in the flame of a blast lamp so that it will fit the condenser tube. It should also be bent down through a slight angle at a short distance from the end so that, when the still is set up, the tube of the retort will incline slightly upward, causing the spray from the retort to run back and so that the short portion of the tube beyond the bend will dip to the incline of the condenser. In making the union between the retort and condenser, the ends of the tubes should come quite close together, the union being made with a stout piece of rubber tubing.

The special reagents used in these determinations are ammonia-free water, Nessler reagent and standard ammoniun chloride solution. The ammonia-free water is prepared by acidifying ordinary distilled water with sulfuric acid and distilling, rejecting the first 50 c.c. of the distillate. To prepare the Nessler reagents, dissolve 35 grams of potassium iodide in a 2,000-c.c. flask with 100 c.c. of water. Dissolve 17 grams of mercuric chloride with 300 c.c.

of water; pour this into the iodide solution, shaking the latter, until a permanent red precipitate forms, add 600 c.c. of a 20 per cent solution of sodium hydroxide and then add more of the mercuric chloride solution until a permanent precipitate is produced. Allow the solution to stand for several days, and decant the clear solution for use. The reagent must be kept in a corked bottle. It improves on keeping. To prepare the standard ammonium chloride, dissolve 1.5683 grams of pure ammonium chloride and make up the volume to 500 c.c. with ammonia-free water. Take 10 c.c. of this solution and dilute to 1,000 c.c. This is the standard ammonia solution, of which 1 c.c. equals 0.00001 gram of ammonia (NH_3).

Free Ammonia.—Pour into a Nessler comparison tube 50 c.c. of the water, and into another tube 50 c.c. of ammonia-free water, with the addition of 0.1 c.c. of the standard ammonia solution. Then add to each tube 2 c.c. of Nessler reagent, and stir them well. If, after standing for a few minutes, the colors are about the same, take 500 c.c. of the water for the determination, and if the sample shows a much darker or lighter color than the standard, take a proportionately greater or less amount for the determination.

Pour into the retort a solution of 1 gram of sodium carbonate in 250 c.c. of water, and distil until the solution is free from ammonia. This is ascertained by testing portions of the distillate with the Nessler reagent. Cool the solution in the retort, and introduce the requisite amount of the water to be examined. Again start the distillation, catching the distillate in 50-c.c. Nessler tubes. To the tube containing the first 50 c.c. add 2 c.c. of the Nessler reagent; stir it well, and place the tube on a white tile. Take 0.4 c.c. of the standard ammonium chloride solution, dilute to the mark in another tube, mix in the Nessler reagent and, after the two solutions have stood for a few minutes, compare the colors. If the standard is darker, pour out 25 c.c., dilute again to 50 c.c. and compare. If necessary, repeat this operation until the colors agree. If the standard is lighter than the sample, discard it, and try the comparison with a larger portion. Compare the second and third 50-c.c. portions of the distillate in the same way, continuing the distillation until a portion is obtained that is free from ammonia. The ammonia in the combined distillate is equal to that contained in the total amount of the standard for the different portions.

Albuminoid Ammonia.—Prepare an alkaline potassium permanganate solution by dissolving 10 grams of potassium hydroxide and 0.5 gram of potassium permanganate in 50 c.c. of water. Boil the solution down to 25 c.c., and dilute to the original volume with ammonia-free water.

Cool the residue of water in the retort; add the alkaline permanganate solution, and make up the volume of the liquid to about 500 c.c. with ammonia-free water. Carry out the distillation and comparisons as in the determination of free ammonia.

DETERMINATION OF NITRITE

The reagents required are sulfanilic acid solution, made by dissolving 1 gram of sulfanilic acid with 300 c.c. of acetic acid (1:4); amidonaphthalene acetate, prepared by boiling 0.2 gram of alpha-naphthylamine with strong acetic acid, filtering and diluting to 400 c.c. with dilute acetic acid, and standard sodium nitrite solution, prepared by dissolving 0.1098 gram of silver nitrite in 100 c.c. of water, adding to this a slight excess of sodium chloride and making up the volume to 1,000 c.c. One cubic centimeter of this solution will contain 0.00001 gram of nitrogen as nitrite.

Take 25 c.c. of the water in a Nessler tube, and mix it with 2 c.c. each of sulfanilic acid and amidonaphthalene acetate solutions. Transfer to another tube 25 c.c. of distilled water and 0.2 c.c. of standard nitrite solution; stir in the reagents, and after allowing the solutions in both tubes to stand a few minutes, compare the colors. Change the standard by diluting it or by adding more of the sodium nitrite until the colors agree. Repeat the test, using the amount of standard nitrite required in the preliminary test, and repeat the operation with the use of more or less of the standard until the colors agree when the two solutions are treated at the same time. Simultaneous treatment of the two is essential.

DETERMINATION OF NITRATE

Prepare a solution of phenyl-hydrogen sulfate by thoroughly mixing 6 grams of pure phenol with 3 c.c. of water and 37 c.c. of strong sulfuric acid. Prepare a standard potassium nitrate solution by heating potassium nitrate in a crucible just to the fusion point, dissolving exactly 0.722 gram of this in water and making up the volume of the solution to a liter. One cubic centimeter contains 0.0001 gram of nitrogen as nitrate.

Take 25 c.c. of the water in a small porcelain dish, transfer to another dish 1 c.c. of the standard nitrate solution and 24 c.c. of pure water, evaporate both solutions to dryness on the water-bath, add to each dish 1 c.c. of the phenyl-hydrogen sulfate solution and mix with small glass rods. When the dishes are cold add to each 1 c.c. of distilled water, then add 3 drops of strong sulfuric acid, mix, then remove the rods, rinsing them with distilled water. Heat the solutions on the water-bath for a few minutes, add to each 25 c.c. of pure water, make ammoniacal and transfer to 250-c.c. graduated cylinders with glass stoppers. Dilute the solutions to 100 c.c., pour the one showing the lightest color into a Nessler tube and dilute the other with water until, after mixing and pouring out 100 c.c. into another Nessler tube, the colors agree. The nitrogen as nitrate is found as follows:

$$\text{Nitrogen per 1,000 c.c.} = \frac{0.004 \times \text{number c.c. of sample after diluting}}{\text{number of c.c. of standard after diluting}}.$$

LIME AND SODA ASH REQUIRED FOR SOFTENING

To determine the amount of lime and soda ash to add to soften the water, proceed as follows:

Put in a 250-c.c. Jena flask 200 c.c. of the water to be tested, add 50 c.c. of saturated lime water and heat to boiling. Cool, shake well and filter through a rapid filter, wash three times with pure, freshly boiled water, and titrate the filtrate with 0.0357N HCl, using methyl orange as indicator. Treat 200 c.c. of freshly boiled distilled water in exactly the same way, being careful to use the same amount of methyl orange in both cases and to finish at the same depth of color. The number of cubic centimeters of standard HCl used the second time, minus the number of cubic centimeters used the first time, multiplied by 5 gives the parts of lime to add to a million parts of water.

Now add to the titrated water in a porcelain dish 30 c.c. of 0.0714N Na_2CO_3, heat to boiling, cool, filter and titrate the excess of soda. The sodium carbonate precipitates both the $CaCl_2$ made in the first titration and the $CaSO_4$, etc., in the water. Therefore, to calculate the amount of sodium carbonate necessary to soften the water, subtract from $2 \times 30 = 60$, the total amount of 0.0357N HCl that has been used in both titrations and multiply by 9.45.

Methyl Orange Solution.—Dissolve 0.025 gram of the sodium salt in 100 c.c. of water and add 0.7 c.c. of 0.10N HCl.

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Calculation of the Results.—In stating the results of the analysis it is customary to combine the acids and the bases in the following manner: The alkalies are first combined with the chlorine, any excess being then combined with the sulfuric acid. Should there be more chlorine than will combine with the alkalies, the excess is calculated first to the calcium and when that is used up, to the magnesium. Should there be alkalies more than sufficient to saturate both the chlorine and the sulfuric acid, the excess is estimated as carbonate.

The sulfuric acid left after the alkalies are satisfied is then united with the calcium and any excess combined with the magnesium.

All the calcium and magnesium not required for the chlorine and the sulfuric acid are then calculated as carbonates.

This order can be departed from where there is reason for some other combination. In water that has been treated with lime and soda to remove the lime, magnesia is frequently present as hydroxide. In estimating the effect of the magnesia compounds in causing corrosion in boilers, all the chlorine and the sulfuric acid in excess of that required to saturate the alkalies should be considered as combined with the magnesia. The table at the end of the book will be found useful in making these calculations.

The analysis should be reported in parts per million and in grains per gallon. To convert parts per million to grains per gallon multiply by 0.058353.

Instead of reporting as above it is often preferred to report as the ions or as the oxides without making assumptions as to the combinations of the oxides or un-ionized molecules.

CHAPTER XLVI

CALCULATION OF NORMAL SOLUTIONS

A normal solution, as used in this book, is a solution a liter of which contains 1 *gram atomic weight of active hydrogen or its equivalent.* Thus a normal solution of HCl will contain 1.008 grams of hydrogen, or 36.468 grams of HCl in a liter, a liter of normal H_2SO_4 will contain 1.008 grams of hydrogen, or 49.034 grams of H_2SO_4. A liter of normal NaOH contains 1.008 grams of hydrogen, or 40.008 grams of NaOH, and a liter of normal NH_4OH contains 1.008 grams of *hydroxyl hydrogen,* or 35.05 grams of NH_4OH. If an acid such as H_3PO_4 is used in a reaction wherein only two of its hydrogen atoms are active acid ions, a normal solution will contain one-half of the gram molecular weight of phosphoric acid in a liter, while if in the reaction all three of the hydrogen atoms are active, a liter of normal phosphoric acid solution will contain one-third of the gram atomic weight of phosphoric acid. That is, the amount of an acid or alkali contained in a liter of a normal solution depends upon the reaction for which the reagent is to be used, but it will always contain 1 gram atomic weight of hydrogen which will take part in the given reaction.

With oxidizing and reducing solutions the same principle holds good. For instance, 1 gram molecular weight of $KMnO_4$ in an acid solution will give up oxygen sufficient to oxidize 5.04 grams of hydrogen; therefore, a normal solution of permanganate when it is to be used in an acid solution will contain one-fifth of the gram molecular weight of $KMnO_4$ per liter. In an alkaline solution, 1 gram molecular weight of $KMnO_4$ will only oxidize the equivalent of 3.024 grams of hydrogen; therefore, when it is to be used in an alkaline solution (as in the Volhard method for manganese) a liter of normal solution will contain one-third of the gram molecular weight of $KMnO_4$.

In making up normal solutions (or fractional normal solutions) of oxidizing or reducing reagents it is most convenient to consider the change in valence which the reagent undergoes. Thus, when permanganate is used to titrate iron, as given on page 36, the manganese undergoes a change of valence from 7 to 2, that is, a normal permanganate solution contains one-fifth of its gram molecular weight in a liter. In the Volhard process, the manganese undergoes a change of valence of 3 and a normal permanganate solution for use in the Volhard titration contains one-third of its gram molecular weight in a liter. Similarly, when $K_2Cr_2O_7$ is used to titrate iron as directed on page 31, the chromium atoms undergo a change of valence of 3 each or 6 together. Therefore, a normal solution of $K_2Cr_2O_7$ contains one-sixth of the gram molecular weight of $K_2Cr_2O_7$ in a liter.

When iron is titrated with an oxidizing agent, it undergoes a change in valence of one. Therefore, a liter of a normal solution of an oxidizing agent, as permanganate, will oxidize the gram atomic weight of iron, or 55.84 grams, and 1 c.c. will oxidize 0.05584 gram of iron and 1 c.c. of a 0.10N solution will oxidize (or titrate) 0.005584 gram of iron. The calculation for vanadium, manganese, chromium, etc. is done in the same way, remembering that the atomic weight of the element is divided by its change in valence.

When phosphorus is determined by the Emmerton process, the valence of the $(NH_4)_3PO_4 12MoO_3$ is reduced by 34; that is, a gram molecular weight of the "yellow precipitate" is reduced by the action of 34 grams of hydrogen, and when it is oxidized back by the standard permanganate, enough permanganate must be used to oxidize the same amount of hydrogen or raise the valence of the reduced "yellow precipitate" molecule 34. Therefore, a liter of a normal permanganate is equal to the gram atomic weight of phosphorus divided by 34 and 1 c.c. of a 0.10N permanganate is equal to $31.04 \div 34 \times 10 \times 1{,}000$ grams, or 0.000091294 gram phosphorus.

The use of normal solutions (or fractional normal solutions) greatly simplifies calculations. Of a normal acid 1 c.c. will exactly neutralize 1 c.c. of a normal alkali, and 1 c.c. of a normal oxidizing solution will exactly oxidize 1 c.c. of a normal reducing solution (if they are capable of reacting with each other).

TABLE 1.—INTERNATIONAL ATOMIC WEIGHTS, 1921

	Symbol	Atomic weight		Symbol	Atomic weight
Aluminium	Al	27.100	Molybdenum	Mo	96.000
Antimony	Sb	120.200	Neodymium	Nd	144.300
Argon	A	39.000	Neon	Ne	20.200
Arsenic	As	74.960	Nickel	Ni	58.680
Barium	Ba	137.370	Niton (radium emanation)	Nt	222.400
Bismuth	Bi	208.000	Nitrogen	N	14.008
Boron	B	10.900	Osmium	Os	190.900
Bromine	Br	79.920	Oxygen	O	16.000
Cadmium	Cd	112.400	Palladium	Pd	106.700
Caesium	Cs	132.810	Phosphorus	P	31.040
Calcium	Ca	40.070	Platinum	Pt	195.200
Carbon	C	12.005	Potassium	K	39.100
Cerium	Ce	140.250	Praseodymium	Pr	140.900
Chlorine	Cl	35.460	Radium	Ra	226.000
Chromium	Cr	52.000	Rhodium	Rh	102.900
Cobalt	Co	58.970	Rubidium	Rb	85.450
Columbium	Cb	93.100	Ruthenium	Ru	101.700
Copper	Cu	63.570	Samarium	Sa	150.400
Dysprosium	Dy	162.500	Scandium	Sc	45.100
Erbium	Er	167.700	Selenium	Se	79.200
Europium	Eu	152.000	Silicon	Si	28.300
Fluorine	F	19.000	Silver	Ag	107.880
Gadolinium	Gd	157.300	Sodium	Na	23.000
Gallium	Ga	70.100	Strontium	Sr	87.630
Germanium	Ge	72.500	Sulphur	S	32.060
Glucinum	Gl	9.100	Tantalum	Ta	181.500
Gold	Au	197.200	Tellurium	Te	127.500
Helium	He	4.000	Terbium	Tb	159.200
Holmium	Ho	163.500	Thallium	Tl	204.000
Hydrogen	H	1.008	Thorium	Th	232.150
Indium	In	114.800	Thulium	Tm	168.500
Iodine	I	126.920	Tin	Sn	118.700
Iridium	Ir	193.100	Titanium	Ti	48.100
Iron	Fe	55.840	Tungsten	W	184.000
Krypton	Kr	82.920	Uranium	U	238.200
Lanthanum	La	139.000	Vanadium	V	51.000
Lead	Pb	207.200	Xenon	Xe	130.200
Lithium	Li	6.940	Ytterbium (Neoytterbium)	Yb	173.500
Lutecium	Lu	175.000	Yttrium	Yt	89.330
Magnesium	Mg	24.320	Zinc	Zn	65.370
Manganese	Mn	54.930	Zirconium	Zr	90.600
Mercury	Hg	200.600			

TABLE 2.—TABLE OF CHEMICAL FACTORS
(Calculated from 1913 Atomic Weights)

Sought	Found	Factor	Sought	Found	Factor
Ag	$AgCl$	0.7526	Cd	CdS	0.7780
	$AgBr$	0.5744		CdO	0.8754
	AgI	0.4595		$CdSO_4$	0.5392
Ag_2O	$AgCl$	0.8084	CdO	CdS	0.8888
Al	Al_2O_3	0.5303		$CdSO_4$	0.6159
	$AlPO_4$	0.2219	CdS	CdO	1.1252
Al_2O_3	$AlPO_4$	0.4184		$CdSO_4$	0.6930
As	As_2S_3	0.6091	Cl	$AgCl$	0.2474
	As_2S_5	0.4832		Ag	0.3287
	$Mg_2As_2O_7$	0.4827	HCl	$AgCl$	0.2544
	$Mg_2P_2O_7$	0.6734	HCl	Ag	0.3380
As_2O_3	As_2S_3	0.8041	ClO_3	$AgCl$	0.5823
	As_2S_5	0.6378		KCl	1.1194
	$Mg_2As_2O_7$	0.6372		$NaCl$	1.4276
	$Mg_2P_2O_7$	0.8890	ClO_4	$AgCl$	0.6939
AsO_3	As_2S_3	0.9992		KCl	1.3339
	As_2S_5	0.7926		$NaCl$	1.7013
	$Mg_2As_2O_7$	0.7919	CN	$AgCN$	0.1943
As_2O_5	As_2S_3	0.9341		Ag	0.2411
	As_2S_5	0.7410	$HCNS$	$AgCNS$	0.3560
	$Mg_2As_2O_7$	0.7403		$CuCNS$	0.4857
B	B_2O_3	0.3143		$BaSO_4$	0.2531
BO_2	B_2O_3	1.2286	Co	$CoSO_4$	0.3804
BO_3	B_2O_3	1.6875	CoO	$CoSO_4$	0.4834
B_4O_7	B_2O_3	1.1143	Cr	Cr_2O_3	0.6842
Ba	$BaSO_4$	0.5885		$PbCrO_4$	0.1609
	$BaCrO_4$	0.5422		$BaCrO_4$	0.2052
	$BaSiF_6$	0.4912		$K_2Cr_2O_7$	0.3535
BaO	$BaSO_4$	0.6570	Cr_2O_3	$PbCrO_4$	0.2352
	$BaCrO_4$	0.6053		$BaCrO_4$	0.3000
	$BaSiF_6$	0.5484		$K_2Cr_2O_7$	0.5167
Bi	Bi_2O_3	0.8965	CrO_3	Cr_2O_3	1.3158
	$BiAsO_4$	0.5994		$PbCrO_4$	0.3095
	$BiOCl$	0.8017		$BaCrO_4$	0.3947
Bi_2O_3	Bi	1.1154	Cu	CuO	0.7989
	$BiOCl$	0.8942		Cu_2S	0.7986
Br	Ag	0.7408		$CuCNS$	0.5226
	$AgBr$	0.4256		$CuSO_4 5H_2O$	0.2545
	$AgCl$	0.5575	CuO	Cu_2S	0.9996
C	CO_2	0.2727		Cu	1.2517
CO_3	CO_2	1.3636	F	CaF_2	0.4868
Ca	CaO	0.7146		$CaSO_4$	0.2792
	$CaCO_3$	0.4004	SiF_6	CaF_2	0.6074
	$CaSO_4$	0.2943	Fe	Fe_2O_3	0.6994
	CaF_2	0.5133		$(NH_4)_2Fe$	
CaO	$CaCO_3$	0.5603		$(SO_4)_2 6H_2O$	0.1424
	$CaSO_4$	0.4118	FeO	Fe_2O_3	0.8998
	CaF_2	0.7182	FeO	Fe	1.2865
$CaCO_3$	CaO	1.7847	Fe_2O_3	Fe	1.4298
	$CaSO_4$	0.7350	Fe_3O_4	Fe	1.3890

TABLE 2.—TABLE OF CHEMICAL FACTORS—(*Continue*
(Calculated from 1913 Atomic Weights)

Sought	Found	Factor	Sought	Found	Factor
H.........	H_2O	0.1119	N_2O_5......	NO	1.7997
Hg........	HgCl	0.8494		NH_3	3.1707
	HgS	0.8618		$(NH_4)_2PtCl_6$	0.2433
I..........	AgI	0.5406	P..........	$Mg_2P_2O_7$	0.2787
	AgCl	0.8855		$(NH_4)_3PO_4$, $12MoO_3$	0.0165
K........	KCl	0.5244		$P_2O_524MoO_3$	0.0172
	K_2SO_4	0.4487	P_2O_5.......	$Mg_2P_2O_7$	0.6379
	$KClO_4$	0.2822		$(NH_4)_3PO_412MoO_3$	0.0378
	K_2PtCl_6	0.1609		P	2.2887
KCl.......	K_2SO_4	0.8557	Pb........	PbO	0.9283
	$KClO_4$	0.5381		PbS	0.8659
KCl... ...	K_2PtCl_6	0.3068		PbO_2	0.8661
K_2O.......	KCl	0.6317		$PbSO_4$	0.6831
	K_2SO_4	0.5405		$PbCrO_4$	0.6410
	$KClO_4$	0.3399		$PbCl_2$	0.7449
	K_2PtCl_6	0.1938	PbO......	PbO_2	0.9331
Li.........	Li_2SO_4	0.1262		$PbSO_4$	0.7359
	LiCl	0.1637		PbCrO	0.6905
Li_2O.......	Li_2SO_4	0.2718	Pt.........	K_2PtCl_6	0.4015
	LiCl	0.3524	S..........	$BaSO_4$	0.1374
Mg........	MgO	0.6032	SO_2.......	$BaSO_4$	0.2745
	$MgSO_4$	0.2020	SO_3.......	$BaSO_4$	0.3430
	$Mg_2P_2O_7$	0.2184	SO_4.......	$BaSO_4$	0.4115
MgO......	$MgSO_4$	0.3349	SO_4H_2.....	$BaSO_4$	0.4202
	$Mg_2P_2O_7$	0.3622	H_2S.......	$BaSO_4$	0.1460
$MgCO_3$....	$Mg_2P_2O_7$	0.7572	Sb........	Sb_2O_4	0.7897
Mn........	$MnSO_4$	0.3638		Sb_2S_3	0.7142
	MnS	0.6314	Sn........	SnO_2	0.7881
	Mn_3O_4	0.7203	Si.........	SiO_2	0.4693
	$Mn_2P_2O_7$	0.3869	Sr.........	SrO	0.8456
MnO......	$MnSO_4$	0.4697		$SrCO_3$	0.5936
	MnS	0.8153		$SrSO_4$	0.4770
	Mn_3O_4	0.9301		$Sr(NO_3)_2$	0.4140
	$Mn_2P_2O_7$	0.4996	SrO.......	$SrCO_3$	0.7019
Mo........	MoO_3	0.6667		$SrSO_4$	0.5641
	$PbMoO_4$	0.2616		$Sr(NO_3)_2$	0.4896
N.........	NH_3	0.8225			
	NH_4Cl	0.2619	Th........	ThO_2	0.8790
	$(NH_4)_2PtCl_6$	0.0631	Ti.........	TiO_2	0.6005
Na_2O	NaCl	0.5303	U.........	U_3O_8	0.8482
NH_3.......	NH_4Cl	0.3182		UO_2	0.8817
	$(NH_4)_2PtCl_6$	0.0767		$U_2P_2O_7$	0.7326
Ni........	NiO	0.7858	V.........	V_2O_5	0.5614
	$NiC_8H_{14}N_4O_4$	0.2032	W.........	WO_3	0.7931
	$NiSO_4$	0.3792	Zn........	ZnS	0.6709
NO_3H.....	NO	2.0999		ZnO	0.8034
	NH_3	3.6995		$Zn_2P_2O_7$	0.4289
	$(NH_4)_2Cl_6Pt$	0.2839	Zr.........	ZrO_2	0.7390

TABLE 3.—SPECIFIC GRAVITY OF HCl, HNO_3, AND H_2SO_4 AT 15° IN VACUO[1]

Sp. gr.	Per cent by weight			Sp. gr.	Per cent by weight	
	HCl	HNO_3	H_2SO_4		H_2SO_4	
1.000	0.16	0.10	0.09	1.570	66.09	
1.010	2.14	1.90	1.57	1.580	66.95	
1.020	4.13	3.70	3.03	1.590	67.83	
1.030	6.15	5.50	4.49	1.600	68.70	
1.040	8.16	7.26	5.96	1.610	69.56	
1.050	10.17	8.99	7.37	1.620	70.42	
1.060	12.19	10.67	8.77	1.630	71.27	
1.070	14.17	12.32	10.19	1.640	72.12	
1.080	16.15	13.94	11.60	1.650	72.96	
1.090	18.11	15.52	12.99	1.660	73.81	
1.100	20.01	17.10	14.35	1.670	74.66	
1.110	21.92	18.66	15.71	1.680	75.50	
1.120	23.82	20.22	17.01	1.690	76.38	
1.130	25.75	21.76	18.31	1.700	77.17	
1.140	27.66	23.30	19.61	1.710	78.04	
1.150	29.57	24.83	20.91	1.720	78.92	
1.160	31.52	26.35	22.19	1.730	79.80	
1.170	33.46	27.87	23.47	1.740	80.68	
1.180	35.39	29.37	24.76	1.750	81.56	
1.190	37.23	30.87	26.04	1.760	82.44	
1.200	39.11	32.34	27.32	1.770	83.51	
1.210		33.80	28.58	1.780	84.50	
1.220		35.26	29.84	1.790	85.70	
1.230		36.76	31.11	1.800	86.92	
1.240		38.27	32.28	1.810	88.30	
1.250		39.80	33.43	1.820	90.05	
1.260		41.32	34.57	1.830	92.10	
1.270		42.85	35.71	1.840	95.70	
1.280		44.39	36.87	1.841	96.38	
1.290		45.93	38.03	1.8415	97.35	
1.300		47.47	39.19	1.841	98.20	
1.310		49.05	40.35	1.840	98.72	
1.320		50.69	41.50	1.839	99.12	
1.330		52.34	42.66			
1.340		54.04	43.74			
1.350		55.76	44.82			
1.360		57.54	45.88			
1.370		59.36	46.94			
1.380		61.24	48.00			
1.390		63.20	49.06			
1.400		65.27	50.11			
1.410		67.47	51.15			
1.420		69.77	52.15			
1.430		72.14	53.11			
1.440		74.64	54.07			
1.450		77.24	55.03			
1.460		79.94	55.97			
1.470		82.86	56.90			
1.480		86.01	57.83			
1.490		89.86	58.74			
1.500		94.04	59.70			
1.510		98.05	60.65			
1.520		99.62	61.59			
1.530			62.53			
1.540			63.43			
1.550			64.26			
1.560			65.20			

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[1] LUNGE-BERL, Chem. tech. Untersungsmethoden, 6th ed., vol. 1.

TABLE 4.—SPECIFIC GRAVITY OF KOH, NaOH, AND NH_3 SOLUTIONS AT 15° C.

Sp. gr.	Per cent KOH	Per cent NaOH	Sp. gr.	Per cent NH_3
1.007	0.9	0.59	1.000	0.00
1.022	2.6	1.65	0.996	0.91
1.037	4.5	3.22	0.992	1.84
1.052	6.4	4.50	0.988	2.80
1.067	8.2	5.86	0.984	3.80
1.083	10.1	7.30	0.980	4.80
1.100	12.0	8.78	0.976	5.80
1.116	13.8	10.30	0.972	6.80
1.134	15.7	11.90	0.968	7.82
1.152	17.6	13.50	0.964	8.84
1.171	19.5	15.15	0.960	9.91
1.190	21.4	16.91	0.956	11.03
1.210	23.3	18.71	0.952	12.17
1.231	25.1	20.69	0.948	13.31
1.252	27.0	22.50	0.944	14.46
1.274	28.9	24.48	0.940	15.63
1.297	30.7	26.58	0.936	16.82
1.320	32.7	28.83	0.932	18.03
1.345	34.9	31.20	0.928	19.25
1.370	36.9	33.73	0.924	20.49
1.397	38.9	36.36	0.920	21.75
1.424	40.9	39.06	0.916	23.03
1.453	43.4	42.02	0.912	24.33
1.483	45.8	45.16	0.908	25.65
1.514	48.3	48.41	0.904	26.98
1.546	50.6	.....	0.900	28.33
1.580	53.2	.....	0.896	29.69
1.615	55.9	.....	0.892	31.05
1.634	57.5	.....	0.888	32.50
.....	....	.....	0.884	34.10

TABLE 5.—SPECIFIC GRAVITY OF ACETIC ACID AT 15°C.

Specific gravity	Per cent $H.C_2H_3O_2$	Specific gravity	Per cent $H.C_2H_3O_2$	Specific gravity	Per cent $H.C_2H_3O_2$	Specific gravity	Per cent $H.C_2H_3O_2$
0.9992	0	1.0363	26	1.0623	51	1.0747	76
1.0007	1	1.0375	27	1.0631	52	1.0748	77
1.0022	2	1.0388	28	1.0638	53	1.0748	78
1.0037	3	1.0400	29	1.0646	54	1.0748	79
1.0052	4	1.0412	30	1.0653	55	1.0748	80
1.0067	5	1.0424	31	1.0660	56	1.0747	81
1.0083	6	1.0436	32	1.0666	57	1.0746	82
1.0098	7	1.0447	33	1.0673	58	1.0744	83
1.0113	8	1.0459	34	1.0679	59	1.0742	84
1.0127	9	1.0470	35	1.0685	60	1.0739	85
1.0142	10	1.0481	36	1.0691	61	1.0736	86
1.0157	11	1.0492	37	1.0697	62	1.0731	87
1.0171	12	1.0502	38	1.0702	63	1.0726	88
1.0185	13	1.0513	39	1.0707	64	1.0720	89
1.0200	14	1.0523	40	1.0712	65	1.0713	90
1.0214	15	1.0533	41	1.0717	66	1.0705	91
1.0228	16	1.0543	42	1.0721	67	1.0696	92
1.0242	17	1.0552	43	1.0725	68	1.0686	93
1.0256	18	1.0562	44	1.0729	69	1.0674	94
1.0270	19	1.0571	45	1.0733	70	1.0660	95
1.0284	20	1.0580	46	1.0737	71	1.0644	96
1.0298	21	1.0589	47	1.0740	72	1.0625	97
1.0311	22	1.0598	48	1.0742	73	1.0604	98
1.0324	23	1.0607	49	1.0744	74	1.0580	99
1.0337	24	1.0615	50	1.0746	75	1.0553	100
1.0350	25						

TABLE 6.—SPECIFIC GRAVITY AND PERCENTAGE OF ALCOHOL BY VOLUME (Squib)

Per cent alcohol by volume	Specific gravity at $\frac{15.56^\circ}{15.56^\circ}$C.	Per cent alcohol by volume	Specific gravity at $\frac{15.56^\circ}{15.56^\circ}$C.	Per cent alcohol by volume	Specific gravity at $\frac{15.56^\circ}{15.56^\circ}$C.	Per cent alcohol by volume	Specific gravity at $\frac{15.56^\circ}{15.56^\circ}$C.
1	0.9985	26	0.9698	51	0.9323	76	0.8745
2	0.9970	27	0.9691	52	0.9303	77	0.8721
3	0.9956	28	0.9678	53	0.9283	78	0.8696
4	0.9942	29	0.9665	54	0.9262	79	0.8664
5	0.9930	30	0.9652	55	0.9242	80	0.8639
6	0.9914	31	0.9643	56	0.9221	81	0.8611
7	0.9898	32	0.9631	57	0.9200	82	0.8581
8	0.9890	33	0.9618	58	0.9178	83	0.8557
9	0.9878	34	0.9609	59	0.9160	84	0.8526
10	0.9869	35	0.9593	60	0.9135	85	0.8496
11	0.9855	36	0.9578	61	0.9113	86	0.8466
12	0.9841	37	0.9565	62	0.9090	87	0.8434
13	0.9828	38	0.9550	63	0.9069	88	0.8408
14	0.9821	39	0.9535	64	0.9047	89	0.8373
15	0.9815	40	0.9519	65	0.9025	90	0.8340
16	0.9802	41	0.9503	66	0.9001	91	0.8305
17	0.9789	42	0.9490	67	0.8973	92	0.8272
18	0.9778	43	0.9470	68	0.8949	93	0.8237
19	0.9766	44	0.9452	69	0.8925	94	0.8199
20	0.9760	45	0.9434	70	0.8900	95	0.8164
21	0.9753	46	0.9416	71	0.8875	96	0.8125
22	0.9741	47	0.9396	72	0.8850	97	0.8084
23	0.9728	48	0.9381	73	0.8825	98	0.8041
24	0.9716	49	0.9362	74	0.8799	99	0.7995
25	0.9709	50	0.9343	75	0.8769	100	0.7946

TABLE 7.—REDUCTION OF THE VOLUME OF 0.10N SOLUTIONS TO THE VOLUME AT 20° C. (CORRECTIONS GIVEN IN 0.01 CUBIC CENTIMETERS)

Burette reading	6°	8°	10°	12°	14°	16°	18°	20°	22°	24°	26°	28°	30°
5 c.c.	0	0	0	0	0	0	0	0	0	−0	−1	−1	−1
10 c.c.	+1	+1	+1	+1	+1	0	0	0	0	−1	−1	−2	−2
15 c.c.	+2	+2	+2	+2	+1	+1	0	0	0	−1	−2	−2	−3
20 c.c.	+3	+3	+3	+2	+2	+1	0	0	−1	−2	−2	−3	−4
25 c.c.	+4	+3	+3	+3	+2	+2	+1	0	−1	−2	−3	−4	−5
30 c.c.	+4	+4	+4	+3	+3	+2	+1	0	−1	−2	−4	−5	−6
35 c.c.	+5	+5	+4	+4	+3	+2	+1	0	−1	−3	−4	−6	−7
40 c.c.	+6	+6	+5	+5	+3	+2	+2	0	−2	−3	−5	−6	−8
45 c.c.	+6	+6	+5	+5	+4	+3	+2	0	−2	−4	−5	−7	−9
50 c.c.	+7	+7	+6	+6	+4	+3	+2	0	−2	−4	−6	−8	−10

TABLE 8.—DENSITY OF WATER AT 0° TO 36°

Weight in grams of 1 c.c. of water free from air at temperatures of 0 to 36 C. by the hydrogen thermometer—According to Thiesen, Scheel, and Diesselhorst Wiss. Abh. d. Phys.—Techn. Reichsanat. 3, 68, 1900

Degrees	Tenths of degrees									
	0	.1	.2	.3	.4	.5	.6	.7	.8	.9
0	0.999868	874	881	887	893	899	905	911	916	922
1	927	932	936	941	945	950	954	957	961	965
2	968	971	974	977	980	982	985	987	989	991
3	992	994	995	996	997	998	999	999	*000	*000
4	1.000000	000	000	*999	*999	*998	*997	*996	*995	*993
5	0.999992	990	988	986	984	982	979	977	974	971
6	986	965	962	958	954	951	947	943	938	934
7	929	925	920	915	910	904	899	893	888	882
8	876	870	864	857	851	844	837	830	823	816
9	808	801	793	785	778	769	761	753	744	736
10	727	718	709	700	691	681	672	662	652	642
11	632	622	612	601	591	580	569	558	547	536
12	525	513	502	490	478	466	454	442	429	417
13	404	391	379	366	353	339	326	312	299	285
14	271	257	243	229	215	200	186	171	156	141
15	126	111	096	081	065	050	034	018	002	*986
16	0.998970	953	937	920	904	887	870	853	836	819
17	801	784	766	749	731	713	695	677	659	640
18	622	603	585	566	547	528	509	490	471	451
19	432	412	392	372	352	332	312	292	271	251
20	230	210	189	168	147	126	105	083	062	040
21	019	*997	*975	*953	*931	*909	*887	*864	*842	*819
22	0.997797	774	751	728	705	682	659	635	612	588
23	565	541	517	493	469	445	421	396	372	347
24	323	298	273	248	223	198	173	147	122	096
25	071	045	019	*994	*968	*941	*915	*889	*863	*836
26	0.996810	783	756	730	703	676	648	621	594	567
27	539	512	484	456	428	400	372	344	316	288
28	259	231	202	174	145	116	087	058	029	000
29	0.995971	941	912	882	853	823	793	763	733	703
30	673	643	613	582	552	521	491	460	429	398
31	367	336	305	273	242	211	179	148	116	084
32	052	020	*988	*956	*924	*892	*859	*827	*794	*762
33	0.994729	696	663	630	597	564	531	498	464	431
34	398	364	330	296	263	229	195	161	126	092
35	058	023	*989	*954	*920	*885	*850	*815	*780	*745

TABLE 9.—TENSION OF WATER VAPOR ACCORDING TO REGNAULT

Degrees C.	Tension in millimeters	Degrees C.	Tension in millimeters	Degrees C.	Tension in millimeters
1	4.940	13	11.162	25	23.550
2	5.302	14	11.908	26	24.988
3	5.687	15	12.699	27	26.505
4	6.097	16	13.536	28	28.101
5	6.534	17	14.421	29	29.782
6	6.998	18	15.357	30	31.548
7	7.492	19	16 346	31	33.405
8	8.017	20	17.391	32	35.359
9	8.574	21	18.495	33	37.410
10	9.165	22	19.659	34	39.565
11	9.792	23	20.888	35	41.827
12	10.457	24	22.184		

TABLE 10.—VOLUME OF GAS AT 0°C. AND 760 MM. EQUIVALENT TO 1 LITER AT OBSERVED TEMPERATURE AND PRESSURE, MM. HG.

Based upon absolute zero = −273.000°C. Ohio State University School of Mines

Temp., °C.	700	702	704	706	708	710	712	714	716	718	720
0°	.9211	.9237	.9263	.9290	.9316	.9342	.9368	.9395	.9421	.9447	.9474
2°	.9144	.9170	.9186	.9222	.9248	.9274	.9300	.9326	.9353	.9379	.9405
4°	.9078	.9103	.9129	.9155	.9181	.9207	.9233	.9259	.9285	.9311	.9337
6°	.9013	.9038	.9064	.9090	.9116	.9141	.9167	.9193	.9219	.9244	.9270
8°	.8948	.8974	.8999	.9025	.9051	.9076	.9102	.9127	.9153	.9179	.9204
10°	.8885	.8911	.8936	.8961	.8987	.9012	.9038	.9063	.9088	.9114	.9139
12°	.8823	.8848	.8873	.8898	.8924	.8949	.8974	.8999	.9024	.9050	.9075
14°	.8761	.8786	.8811	.8836	.8861	.8886	.8911	.8936	.8962	.8987	.9012
16°	.8701	.8725	.8750	.8775	.8800	.8825	.8850	.8875	.8899	.8924	.8949
18°	.8641	.8666	.8691	.8715	.8740	.8764	.8789	.8814	.8838	.8863	.8888
20°	.8582	.8606	.8631	.8655	.8680	.8704	.8729	.8753	.8778	.8802	.8827
22°	.8524	.8548	.8572	.8597	.8621	.8645	.8670	.8694	.8718	.8743	.8767
24°	.8466	.8491	.8515	.8539	.8563	.8587	.8611	8636	.8660	.8684	.8708
26°	.8410	.8434	.8458	.8482	.8506	.8530	.8554	.8578	.8602	.8626	.8650
28°	.8354	.8378	.8402	.8425	.8449	.8473	.8497	.8521	.8545	.8569	.8593
30°	.8299	.8322	.8346	.8370	.8393	.8417	.8441	.8465	.8488	.8512	.8536
32°	.8244	.8268	.8291	.8315	.8338	.8362	.8386	.8409	.8433	.8456	.8480
34°	.8191	.8214	.8237	.8261	.8284	.8308	.8331	.8354	.8378	.8401	.8425
36°	.8138	.8161	.8184	.8207	.8231	.8254	.8277	.8300	.8324	.8347	.8370
38°	.8085	.8108	.8131	.8154	.8177	.8201	.8224	.8247	.8270	.8293	.8316
40°	.8034	.8056	.8079	.8102	.8125	.8148	.8171	.8194	.8217	.8240	.8263

TABLE 10.—VOLUME OF GAS AT 0°C. AND 760 MM. EQUIVALENT TO 1 LITER AT OBSERVED TEMPERATURE AND PRESSURE, MM. HG.—(*Continued*)

Temp., °C.	722	724	726	728	730	732	734	736	738	740
0°	.9500	.9526	.9553	.9579	.9605	.9632	.9658	.9684	.9711	.9737
2°	.9431	.9457	.9483	.9509	.9535	.9562	.9588	.9614	.9640	.9666
4°	.9363	.9389	.9415	.9441	.9467	.9492	.9518	.9544	.9570	.9596
6°	.9296	.9322	.9347	.9373	.9399	.9425	.9450	.9476	.9502	.9528
8°	.9230	.9255	.9281	.9306	.9332	.9357	.9383	.9409	.9434	.9460
10°	9164	.9190	.9215	.9241	.9266	.9291	.9317	.9342	.9368	.9393
12°	.9100	.9125	.9150	.9176	.9201	.9226	.9251	.9277	.9302	.9327
14°	.9037	.9062	.9087	.9112	.9137	.9162	.9187	.9212	.9237	.9262
16°	.8974	.8999	.9024	.9049	.9074	.9098	.9123	.9148	.9173	.9198
18°	.8912	.8937	.8962	.8987	.9011	.9036	.9061	.9085	.9110	.9135
20°	.8852	.8876	.8901	.8925	.8950	.8974	.8999	.9023	.9048	.9072
22°	.8791	.8816	.8840	.8865	.8889	.8913	.8938	.8962	.8986	.9011
24°	.8732	.8757	.8781	.8805	.8829	.8853	.8878	.8902	.8926	.8950
26°	.8674	.8698	.8722	.8746	.8770	.8794	.8818	.8842	.8866	.8890
28°	.8616	.8640	.8664	.8688	.8712	.8736	.8760	.8783	.8807	.8831
30°	.8559	.8583	.8607	.8631	.8654	.8678	.8702	.8725	.8749	.8773
32°	.8503	.8527	.8550	.8574	.8598	.8621	.8645	.8668	.8692	.8715
34°	.8448	.8471	.8495	.8518	.8542	.8565	.8588	.8612	.8635	.8659
36°	.8393	.8417	.8440	.8463	.8486	.8510	.8533	.8556	.8579	.8603
38°	.8339	.8362	.8385	.8409	.8432	.8455	.8478	.8501	.8524	.8547
40°	.8286	.8309	.8332	.8355	.8378	.8401	.8424	.8447	.8470	.8493

TABLE 10.—VOLUME OF GAS AT 0°C. AND 760 MM. EQUIVALENT TO 1 LITER AT OBSERVED TEMPERATURE AND PRESSURE, MM. HG.—(*Continued*)

Temp., °C.	742	744	746	748	750	752	754	756	758	760
0°	.9763	.9790	.9816	.9842	.9868	.9895	.9921	.9947	.9974	1.0000
2°	.9692	.9718	.9744	.9771	.9797	.9823	.9849	.9875	.9901	.9927
4°	.9622	.9648	.9674	.9700	.9726	.9752	.9778	.9804	.9830	.9856
6°	.9553	.9579	.9605	.9631	.9656	.9682	.9708	.9734	.9759	.9785
8°	.9485	.9511	.9536	.9562	.9588	.9613	.9639	.9664	.9690	.9715
10°	.9418	.9444	.9469	.9494	.9520	.9545	.9571	.9596	.9621	.9647
12°	.9352	.9377	.9403	.9428	.9453	.9478	.9503	.9529	.9554	.9579
14°	.9287	.9312	.9337	.9362	.9387	.9412	.9437	.9462	.9487	.9512
16°	.9223	.9248	.9272	.9297	.9322	.9347	.9372	.9397	.9422	.9446
18°	.9159	.9184	.9209	.9233	.9258	.9283	.9307	.9332	.9357	.9381
20°	.9097	.9121	.9146	.9170	.9195	.9219	.9244	.9268	.9293	.9317
22°	.9035	.9059	.9084	.9108	.9132	.9157	.9181	.9205	.9230	.9254
24°	.8974	.8998	.9023	.9047	.9071	.9095	.9119	.9144	.9168	.9192
26°	.8914	.8938	.8962	.8986	.9010	.9034	.9058	.9082	.9106	.9130
28°	.8855	.8879	.8903	.8927	.8951	.8974	.8998	.9022	.9046	.9070
30°	.8797	.8820	.8844	.8868	.8891	.8915	.8939	.8963	.8986	.9010
32°	.8739	.8762	.8786	.8810	.8833	.8857	.8880	.8904	.8927	.8951
34°	.8682	.8705	.8729	.8752	.8776	.8799	.8822	.8846	.8869	.8893
36°	.8626	.8649	.8672	.8696	.8719	.8742	.8765	.8789	.8812	.8835
38°	.8570	.8593	.8616	.8640	.8663	.8686	.8709	.8732	.8755	.8778
40°	.8516	.8538	.8561	.8584	.8607	.8630	.8653	.8676	.8699	.8722

TABLE 11.—VOLUME OF GAS AT OBSERVED TEMPERATURE AND PRESSURE EQUIVALENT TO 1 LITER AT 0°C. AND 760 MM. MERCURY

Based Upon Absolute Zero = −273.000°C. Ohio State University—School of Mines

Temp., °C.	700	702	704	706	708	710	712	714	716	718	720
0°	1.0857	1.0826	1.0795	1.0765	1.0735	1.0705	1.0674	1.0645	1.0615	1.0585	1.0556
2°	1.0937	1.0906	1.0875	1.0844	1.0813	1.0783	1.0752	1.0722	1.0692	1.0663	1.0633
4°	1.1016	1.0985	1.0954	1.0923	1.0892	1.0861	1.0831	1.0800	1.0770	1.0740	1.0710
6°	1.1096	1.1064	1.1032	1.1001	1.0970	1.0940	1.0909	1.0878	1.0848	1 0818	1.0787
8°	1.1175	1.1144	1.1112	1.1080	1.1049	1.1018	1.0987	1.0956	1.0925	1.0895	1.0865
10°	1.1255	1.1223	1.1191	1.1159	1.1128	1.1096	1.1065	1.1034	1.1003	1.0973	1.0942
12°	1.1334	1.1302	1.1270	1.1238	1.1206	1.1175	1.1144	1.1112	1.1081	1.1050	1.1020
14°	1.1414	1.1382	1.1349	1.1317	1.1285	1.1253	1.1222	1.1190	1.1159	1.1128	1.1097
16°	1.1493	1.1461	1.1428	1.1396	1.1364	1.1332	1.1300	1.1268	1.1237	1.1206	1.1174
18°	1.1573	1.1540	1.1507	1.1475	1.1442	1.1410	1.1378	1.1346	1.1314	1.1283	1.1252
20°	1.1653	1.1620	1.1587	1.1554	1.1521	1.1489	1.1456	1.1424	1.1392	1.1361	1.1329
22°	1.1732	1.1699	1.1665	1.1632	1.1600	1.1567	1.1535	1.1502	1.1470	1.1438	1.1406
24°	1.1812	1.1778	1.1744	1.1711	1.1678	1.1645	1.1612	1.1580	1.1548	1.1516	1.1484
26°	1.1891	1.1858	1.1824	1.1790	1.1757	1.1724	1.1691	1.1658	1.1625	1.1593	1.1561
28°	1.1971	1.1937	1.1903	1.1869	1.1835	1.1802	1.1769	1.1736	1.1703	1.1671	1.1638
30°	1.2050	1.2016	1.1982	1.1948	1.1914	1.1881	1.1847	1.1814	1.1781	1.1748	1.1716
32°	1.2130	1.2095	1.2061	1.2027	1.1993	1.1959	1.1925	1.1892	1.1859	1.1826	1.1793
34°	1.2209	1.2175	1.2140	1.2106	1.2072	1.2038	1.2004	1.1970	1.1937	1.1903	1.1870
36°	1.2288	1.2254	1.2219	1.2185	1.2150	1.2116	1.2082	1.2048	1.2014	1.1981	1.1948
38°	1.2368	1.2333	1.2298	1.2263	1.2229	1.2194	1.2160	1.2126	1.2092	1.2058	1.2025
40°	1.2448	1.2413	1.2377	1.2342	1.2307	1.2273	1.2238	1.2204	1.2170	1.2136	1.2102

TABLE 11.—VOLUME OF GAS AT OBSERVED TEMPERATURE AND PRESSURE EQUIVALENT TO 1 LITER AT 0°C. AND 760 MM. MERCURY—(*Continued*)

Temp., °C.	722	724	726	728	730	732	734	736	738	740
0°	1.0527	1.0497	1.0469	1.0440	1.0411	1.0383	1.0354	1.0326	1.0298	1.0270
2°	1.0604	1.0574	1.0545	1.0516	1.0487	1.0459	1.0430	1.0401	1.0373	1.0345
4°	1.0681	1.0651	1.0622	1.0593	1.0564	1.0535	1.0506	1.0478	1.0449	1.0421
6°	1.0758	1.0728	1.0698	1.0669	1.0640	1.0611	1.0582	1.0553	1.0524	1.0496
8°	1.0835	1.0805	1.0775	1.0745	1.0716	1.0687	1.0658	1.0629	1.0600	1.0571
10°	1.0912	1.0882	1.0852	1.0822	1.0792	1.0763	1.0733	1.0704	1.0675	1.0646
12°	1.0989	1.0959	1.0929	1.0899	1.0869	1.0839	1.0809	1.0780	1.0751	1.0722
14°	1.1066	1.1036	1.1005	1.0975	1.0945	1.0915	1.0885	1.0856	1.0826	1.0797
16°	1.1143	1.1113	1.1108	1.1051	1.1021	1.0991	1.0961	1.0932	1.0902	1.0872
18°	1.1220	1.1189	1.1159	1.1128	1.1097	1.1067	1.1037	1.1007	1.0977	1.0948
20°	1.1298	1.1267	1.1235	1.1204	1.1174	1.1143	1.1113	1.1083	1.1053	1.1023
22°	1.1375	1.1343	1.1312	1.1281	1.1250	1.1219	1.1189	1.1158	1.1128	1.1098
24°	1.1452	1.1420	1.1389	1.1357	1.1326	1.1295	1.1264	1.1234	1.1203	1.1173
26°	1.1529	1.1497	1.1465	1.1434	1.1403	1.1371	1.1340	1.1310	1.1279	1.1248
28°	1.1606	1.1574	1.1542	1.1510	1.1479	1.1447	1.1416	1.1385	1.1354	1.1324
30°	1.1683	1.1651	1.1619	1.1587	1.1555	1.1523	1.1492	1.1461	1.1430	1.1399
32°	1.1760	1.1728	1.1696	1.1663	1.1631	1.1600	1.1568	1.1537	1.1505	1.1474
34°	1.1837	1.1805	1.1772	1.1740	1.1708	1.1676	1.1644	1.1612	1.1581	1.1549
36°	1.1915	1.1882	1.1849	1.1816	1.1784	1.1752	1.1720	1.1688	1.1656	1.1625
38°	1.1992	1.1959	1.1925	1.1893	1.1860	1.1828	1.1795	1.1763	1.1732	1.1700
40°	1.2069	1.2035	1.2002	1.1969	1.1936	1.1903	1.1871	1.1839	1.1807	1.1775

TABLE 11.—VOLUME OF GAS AT OBSERVED TEMPERATURE AND PRESSURE EQUIVALENT TO 1 LITER AT 0°C. AND 760 MM. MERCURY—(*Continued*)

Temp., °C.	742	744	746	748	750	752	754	756	758	760
0°	1.0243	1.0215	1.0188	1.0160	1.0133	1.0107	1.0080	1.0053	1.0026	1.0000
2°	1.0318	1.0290	1.0262	1.0235	1.0207	1.0180	1.0153	1.0127	1.0100	1.0073
4°	1.0393	1.0365	1.0337	1.0310	1.0282	1.0255	1.0227	1.0200	1.0173	1.0147
6°	1.0468	1.0439	1.0411	1.0384	1.0356	1.0329	1.0301	1.0274	1.0247	1.0220
8°	1.0543	1.0514	1.0486	1.0458	1.0430	1.0403	1.0375	1.0348	1.0320	1.0293
10°	1.0618	1.0589	1.0561	1.0533	1.0505	1.0477	1.0449	0.0421	1.0393	1.0366
12°	1.0693	1.0664	1.0635	1.0607	1.0579	1.0551	1.0523	1.0495	1.0467	1.0440
14°	1.0768	1.0739	1.0710	1.0681	1.0653	1.0625	1.0597	1.0568	1.0540	1.0513
16°	1.0843	1.0814	1.0785	1.0756	1.0728	1.0699	1.0670	1.0642	1.0614	1.0586
18°	1.0918	1.0889	1.0859	1.0830	1.0801	1.0773	1.0744	1.0716	1.0687	1.0659
20°	1.0993	1.0964	1.0934	1.0905	1.0876	1.0847	1.0818	1.0790	1.0762	1.0733
22°	1.1068	1.1038	1.1009	1.0979	1.0950	1.0921	1.0892	1.0863	1.0834	1.0806
24°	1.1143	1.1113	1.1083	1.1054	1.1024	1.0995	1.0966	1.0937	1.0908	1.0879
26°	1.1218	1.1188	1.1158	1.1128	1.1098	1.1069	1.1040	1.1010	1.0981	1.0952
28°	1.1293	1.1263	1.1232	1.1202	1.1173	1.1143	1.1113	1.1084	1.1055	1.1026
30°	1.1368	1.1338	1.1307	1.1277	1.1247	1.1217	1.1187	1.1158	1.1129	1.1099
32°	1.1443	1.1412	1.1382	1.1351	1.1321	1.1291	1.1261	1.1231	1.1201	1.1172
34°	1.1518	1.1487	1.1456	1.1426	1.1395	1.1365	1.1335	1.1305	1.1275	1.1245
36°	1.1593	1.1562	1.1531	1.1500	1.1470	1.1440	1.1410	1.1379	1.1349	1.1319
38°	1.1668	1.1637	1.1606	1.1575	1.1544	1.1513	1.1483	1.1452	1.1422	1.1392
40°	1.1743	1.1711	1.1680	1.1649	1.1618	1.1587	1.1556	1.1526	1.1495	1.1465

TABLE 12.—CONVERSION FACTORS FOR GAS

Grams per cubic meter × 43.7 = grains per 100 cubic feet.
Grams per cubic meter × 0.437 = grains per cubic foot.
Grains per cubic foot × 2.288 = grams per cubic meter.
Grains per 100 cubic feet × 0.02288 = grams per cubic meter.
Grams per cubic foot × 35.31 = grams per cubic meter.
Grams benzine per cubic meter × 0.0088 = gallons per 1,000 cubic feet.

22.37 liters of any true gas or vapor, at 0°C. and 760 mm. pressure, has a weight in grams equal to its molecular weight. Hence it follows that the molecular weight of any gas or vapor divided by 22.37 gives the weight in kilos of a cubic meter of that gas.

22.35 cu. ft. of any gas at 0°C. and 760. mm. pressure has a weight in ounces equal to its molecular weight. One pound molecular volume at 30″ H_g, 60°F. and saturated with water occupies 386 cu. ft. and when dry it occupies 380 cu. ft. At 32°F. it occupies 359 cu. ft. when dry.

TABLE 13.—PRESSURE EQUIVALENTS

Pounds per square inch	Ounces per inch	Feet water	Inches water	Centimeters water	Inches kerosene	Centimeters kerosene	Inches mercury	Centimeters mercury
1.000	16.000	2.309	27.710	70.480	35.080	89 200	2.040	5.190
0.063	1.000	0.144	1.732	4.405	2.190	5.575	0.127	0.325
0.433	6.928	1.000	12.000	30.360	15.120	38.560	0.888	2.259
0.036	0.576	0.083	1.000	2.530	1.260	3.188	0.074	0.187
0.014	0.224	0.033	0.393	1.000	0.496	1.260	0.029	0.074
0.028	0.448	0.064	0.790	2.030	1.000	2.530	0.058	0.147
0.011	0.170	0.026	0.311	0.790	0.393	1.000	0.023	0.058
0.490	7.840	1.130	13.590	34.380	17.200	43.410	1.000	2.530
0.190	3.040	0.441	5.299	13.590	6.742	17.200	0.392	1.000

1 pound per square inch = 0.0703 kilos per square centimeter. 1 kilo per square centimeter = 14.2232 pounds per square inch.

1 pound per square foot = 4.8825 kilos per square meter. 1 kilo per square meter = 0.2048 pound per square foot.

1 gross ton per square foot = 10.937 metric tons per square meter. 1 metric ton per square meter = 0.091 gross ton per square foot.

1 atmosphere = 14.72 pounds per square inch = 1.0333 kilos per square centimeter.

Kerosene = specific gravity 0.79 (approx. 0.8).

760 millimeters mercury = 14.71 pounds pressure per square inch = 29.94 inches mercury = 33.52 feet water.

30 inches mercury = 761.9 millimeters mercury.

TABLE 14.—CONSTANTS FOR CERTAIN GASES AND VAPORS

(From Gas Chemists' Handbook)

1	2		3	4	5	6	7	8	9	10	11	12
Name of gas or vapor	Formula		Molecular weight	Sp. gr. gas or vapor at 60° F., air = 1.000	Boiling point ° F.	Sp. gr. liquid at 60° F., water = 1.000	Sp. heat eq. wts. at const. pr., water = 1.000	Cubic feet per pound 60°–30″	Weight 1 cu. ft. in pounds	Heat of combustion (gross)		
										Calories per molecular wt. in grams	B.t.u. per cu. ft.	B.t.u. per pound
Carbon to CO	Cx		12.000	0.82920	......	......	......	15.749	0.06350	29,000	138.0	4,325
Carbon to CO_2	Cx		12.000	0.82920	......	......	......	15.749	0.06350	96.960	461.0	14,544
Carbonic oxide	CO		28.000	0.96716	−310.0	......	0.2450	13.550	0.07380	67.960	323.0	4.369
Hydrogen	H_2		2.016	0.06960	−423.4	......	3.4090	188.700	0.00530	68.415	325.0	61,085
Methane	Paraffin series C_nH_{2n+2}	CH_4	16.030	0.55450	−263.2	......	0.5920	23.640	0.04230	211,933	1,008.0	23,798
Ethane		C_2H_6	30.050	1.04940	−128.2	......	......	12.480	0.08010	370,456	1,778.0	22,190
Propane		C_3H_8	44.060	1.52230	− 38.2	0.6130	....	8.610	0.11620	529,205	2,513.0	21 620
Butane		C_4H_{10}	58.080	2.01000	+ 33.0	......	......	6.510	0.15350	687,203	3,269.0	21,298
Pentane		C_5H_{12}	72.100	2.49050	+ 98.6	0.6263	......	5.260	0.19020	847,247	4.022.0	21,152
Hexane		C_6H_{14}	86.110	2.97210	+160.7	0.6630	......	4.400	0.22710	999,220	4,714.0	20,887
Ethylene	Olefin series C_nH_{2n}	C_2H_4	28.030	0.96836	−153.4	......	0.4040	13.530	0.07390	333,361	1,583.0	21,407
Propylene		C_3H_6	42.050	1.45270	− 58.4	......	......	0.020	0.11090	492,742	2,340.0	21,092
Butylene		C_4H_8	56.060	1.23670	+ 23.0	......	......	6.760	0.14790	650.632	3,089.0	20,891
Amylene		C_5H_{10}	70.080	2.42110	+102.0	0.6511	......	5.410	0.18490	807,602	3,835.0	20,743
Acetylene	Acetylene series C_nH_{2n-2}	C_2H_2	26.020	0.90560	−112.0	0.6130	......	14.450	0.06920	310,054	1,483.0	21,449
Allylene		C_3H_4	40.030	1.38230	− 10.3	......	......	9.447	0.10585	467,550	2,227.1	21,040
Crotonylene		C_4H_6	54.050	1.86610	+ 81.0	......	......	6.998	0.14290	593,091	2,822.6	19,752
Benzene	Aromatic series C_nH_{2n-6}	C_6H_6	78.050	2.69530	+176.6	0.8839	0.3754	4.860	0.20590	787,993	3,741.0	18,175
Toluene		C_7H_8	92.060	3.17920	+231.8	0.8714	......	4.120	0.24290	934.409	4,436.0	18,270
Meta-xylene		C_8H_{10}	106.080	3.66300	+282.4	0.8697	......	3.570	0.28000	1,084,986	5,155.0	18,410
Mesitylene		C_9H_{12}	120.100	4.14680	+328.1	0.8583	......	3.149	0.31755	1,282,310	6.108.0	19,235
Naphthalene	$C_{10}H_8$		128.060	4.42300	+424.7	1.1508	......	2.952	0.33870	1,230,657	5,859.0	17,298
Hydrogen sulfide	H_2S		34.090	1.19060	− 79.2	0.9000	0.2423	11.000	0.09090	136,701	657.0	17,218
Ammonia	NH_3		17.020	0.59710	− 37.3	0.6234	0.5202	22.178	0.04509	90,650	432.8	9,598
Hydrocyanic acid	HCN		27.010	0.93480	+ 79.7	0.6967	......	13.968	0.07159	158,620	757.0	10,575
Cyanogen	CN		26.000	1.80000	− 5.8	0.8600	......	7.258	0.13779	259,620	1,238.2	8.986
Carbon bisulfide	CS_2		76.120	2.62980	+114.8	1.2920	0.1590	4.965	0.20139	265,130	1,264.6	6.279
Methyl alcohol	CH_3OH		32.030	1.11210	+131.2	0.8027	0.4580	11.830	0.08450	182,187	865.0	10,238
Ethyl alcohol	C_2H_5OH		46.050	1.58940	+172.9	0.7946	1.4534	8.230	0.12150	340,494	1.617.0	13,309
Carbonic acid	CO_2		44.000	1.52909	−108.4	0.8300	0 2163	8.570	0.11670			
Water	H_2O		18.020	0.62170	+212.0	1.0000	0.4805	21.004	0.04761			
Sulfur dioxide	SO_2		64.070	2.26380	+ 12.6	1.4900	0.1553	5.780	0.17290			
Oxygen	O_2		32.000	1.10550	−294.5	1.1340	0.2174	11.850	0.08440			
Nitrogen	N_2		28.000	0.96740	−320.1	0.8050	0.2438	13.530	0.07390			
Air	......		....	1.00000	....	......	0.2374	13.090	0.07640			

* To get the "net" heat of combustion per gram molecule, subtract 5,335 cal. for each gram atom of hydrogen, or 50.5 B.T.U. per cu. ft. of H_2.

TABLE 14.—CONSTANTS FOR CERTAIN GASES AND VAPORS—(*Continued*)

	13	14	15	16	17	18	19	20	21	22	23	24	25
Name of gas or vapor	Cu. ft. per cu. ft. of gas or vapor					Pounds per pound of gas or vapor					Heat of formation constant pressure		
	Req. for com'n		Products of combustion			Req. for com'n		Products of combustion			Calories per molecular weight in grams	B.t.u.	
	Air	Oxygen	CO_2	H_2O	Nitrogen	Air	Oxygen	CO_2	H_2O	Nitrogen		Per cu. ft.	Per pound
Carbon to CO				...	......	5.771	1.333+		.....	4.438	....		
Carbon to CO_2				...	......	11.541	2.666+		.....	8.875			
Carbonic oxide	2.390	0.50	1.0	...	1.890	2.450	0.570	1.570	.....	1.880	+29,000	+138.4	+1869.2
Hydrogen	2.390	0.50	...	1.0	1.890	34.190	7.940	.....	8.940	26.250			
Methane	9.560	2.00	1.0	2.0	7.560	17.170	3.990	2.740	2.250	13.180	+21,750	+103.1	+2435.6
Ethane	16.720	3.50	2.0	3.0	13.230	16.060	3.750	2.930	1.800	12.330	+28,560	+136.0	+1713.6
Propane	23.890	5.00	3.0	4.0	18.900	15.630	3.630	3.000	1.640	12.000	+35,110	+167.2	+1436.3
Butane	31.060	6.50	4.0	5.0	24.570	15.410	3.580	3.030	1.550	11.830	+42,450	+202.2	+1317.3
Pentane	38.220	8.00	5.0	6.0	30.240	15.280	3.550	3.050	1.500	11.730	+47,850	+227.9	+1196.2
Hexane	45.390	9.50	6.0	7.0	35.910	15.200	3.530	3.070	1.460	11.670	+61,080	+290.9	+1278.4
Ethylene	14.330	3.00	2.0	2.0	11.340	14.720	3.420	3.140	1.290	11.300	− 2,710	− 12.9	− 174.2
Propylene	21.500	4.50	3.0	3.0	17.010	14.720	3.420	3.140	1.290	11.300	+ 3,220	+ 15.3	+ 138.0
Butylene	28.670	6.00	4.0	4.0	22.68	14.720	3.420	3.140	1.290	11.300	+10,660	+ 50.7	+ 342.6
Amylene	35.830	7.50	5.0	5.0	28.350	14.720	3.420	3.140	1.290	11.300	+18,970	+113.7	+ 614.1
Acetylene	11.940	2.50	2.0	1.0	9.450	13.220	3.070	3.380	0.690	10.150	−47,770	−227.5	−3300.7
Allylene	19.140	4.00	3.0	2.0	15.140	13.850	3.200	3.300	0.900	10.650	−39,950	−189.2	−1796.4
Crotonylene	26.320	5.50	4.0	3.0	20.828	14.110	3.260	3.260	1.300	10.850			
Benzene	35.830	7.50	6.0	3.0	28.350	13.220	3.070	3.380	0.690	10.150	−12,510	− 47.3	− 229.3
Toluene	43.000	9.00	7.0	4.0	34.020	13.470	3.130	3.350	0.780	10.340	− 3,520	− 16.7	− 68.8
Meta-xylene	50.170	10.50	8.0	5.0	39.690	13.650	3.170	3.320	0.850	10.480			
Mesitylene	57.420	12.00	9.0	6.0	45.420	13.850	3.200	3.300	0.900	10.650	+ 490	+ 2.3	+ 7.3
Naphthalene	57.420	12.00	10.0	4.0	45.420	12.984	3.000	3.437	0.563	9.984			
Hydrogen sulfide	7.170	1.50	SO_2 1 Vol.	1.0	5.670	6.070	1.410	SO_2 1.88	0.530	4.660	+ 4,740	+ 22.6	+ 250.9

Ammonia........	3.589	0.75	...	1.5	2.889	6.1110	1.412	.....	1.588	5.522	+11,890	+ 56.7	+1259.0
Hydrocyanic acid.	5.981	1.25	1.0	0.5	4.781	6.4100	1.481	1.630	0.333	5.447	−27,480	−131.1	−1832.0
Cyanogen........	9.570	2.00	2.0	...	8.570	5.3230	1.230	1.692	.....	4.631	−65,700	−313.2	−2273.9
Carbon bisulfide...	14.355	3.00	1.0	$\frac{SO_2}{2.0}$	11.355	5.4660	1.263	0.579	$\frac{SO_2}{1.684}$	4.203	−26,010	−124.0	− 616.0
Methyl alcohol....	7.170	1.50	1.0	2.0	5.670	6.4600	1.500	1.370	1.120	4.960	+51,450	+246.4	+2894.0
Ethyl alcohol.....	14.330	3.00	2.0	3.0	11.340	8.9500	2.080	1.910	1.170	6.870	+58,470	+278.5	+2288.0
Carbonic acid.....	......	.....	...	...	......	......	.....	.....	......	......	+97,266	+463.1	+3979.1
Water...........	......	.....	...	...	......	......	.....	.....	.....	......	+68,360	+327.1	+6870.4
Sulphur dioxide...	......	.....	...	...	......	......	.....	.....	.....	......	+71,156	+337.3	+1999.1

The figures were filled in according to the latest and best obtainable data, a few of them were calculated. We used the figures of the Bureau of Mines wherever such figures were available. Where the Bureau of Mines failed to show the figures, we used those of the literature that seemed to be the most up to date data available.

TABLE 15.—THERMAL CAPACITY IN SMALL CALORIES PER GRAM MOLECULAR VOLUME, 0 TO 36°C., GAS AT CONSTANT PRESSURE

Temperature		O_2, CO, N_2	Dif. per °C.	H_2	Dif. per °C.	CO_2 and SO_2	Dif. per °C.	H_2O	Dif. per °C.	CH_4	Dif. per °C.
°C.	°F.										
0	32.0	0.00	...	0.00	....	0.00	....	0.00	....	0.00	
1	33.8	6.77	6.77	6.75	6.75	8.80	8.80	8.46	8.46	9.79	9.79
2	35.6	13.55	6.78	13.49	6.75	17.61	8.81	16.91	8.46	19.58	9.80
3	37.4	20.32	6.78	20.24	6.75	26.43	8.82	25.37	8.45	29.39	9.81
4	39.2	27.10	6.78	26.99	6.75	35.25	8.82	33.82	8.45	39.22	9.82
5	41.0	33.88	6.78	33.74	6.75	44.07	8.83	42.27	8.45	49.05	9.83
6	42.8	40.66	6.78	40.49	6.75	52.91	8.84	50.73	8.45	58 90	9.85
7	44.6	47.44	6.78	47.24	6.75	61.75	8.84	59.18	8.45	68.75	9.86
8	46.4	54.22	6.78	53.99	6.75	70.59	8.85	67.63	8.45	78.62	9.87
9	48.2	61.00	6.78	60.75	6.75	79.44	8.85	76.08	8.45	88.51	9.88
10	50.0	67.78	6.78	67.51	6.75	88.30	8.86	81.53	8.45	98.40	9.89
11	51.8	74.56	6.78	74.26	6.76	97.16	8.87	92.98	8.45	108.31	9.91
12	53.6	81.35	6.79	81.02	6.76	106.03	8.87	101.43	8.45	118.22	9.92
13	55.4	88.13	6.79	87.77	6.76	114.91	8.88	109.88	8.45	128.15	9 93
14	57.2	94.92	6.79	94.53	6.76	123.79	8.88	118.32	8.45	138.10	9.94
15	59.0	101.71	6.79	101.29	6.76	132.68	8.89	126.77	8.45	148.05	9.95
16	60.8	108.50	6.79	108.05	6.76	141.57	8.90	135.22	8.45	158.02	9.97
17	62.6	115.29	6.79	114.81	6.76	150.47	8.90	143.66	8.45	167.99	9.98
18	64.4	122.08	6.79	121.57	6.76	159.38	8.91	152.11	8.45	177.98	9.99
19	66.2	128.87	6.79	128.34	6.76	168.29	8.91	160.55	8.44	187.99	10.00
20	68.0	135.66	6.79	135.16	6.76	177.21	8.92	169.00	8.44	198.00	10.01
21	69.8	142.45	6.79	141.86	6.76	186.13	8.93	177.44	8.44	208.03	10.03
22	71.6	149.25	6.80	148.63	6.77	195.06	8.93	185.88	8.44	218.06	10.04
23	73.4	156.04	6.80	155.39	6.77	203.99	8.94	194.33	8.44	228.11	10.05
24	75.2	162.84	6.80	162.16	6.77	212.94	8.94	202.77	8.44	238.18	10.06
25	77.0	169.64	6.80	168.93	6.77	221.88	8.95	211.21	8.44	248.25	10.07
26	78.8	176.44	6.80	175.70	6.77	230.84	8 96	219.65	8.44	258.34	10.09
27	80.6	183.24	6.80	182.47	6.77	239.80	8.96	228.09	8.44	268.43	10.10
28	82.4	190.04	6.80	189.24	6.77	248.76	8.97	236.53	8.44	278.54	10.11
29	84.2	196.84	6.80	196.01	6.77	257.73	8.97	244.97	8.44	288.67	10.12
30	86.0	203.64	6.80	202.78	6.77	266.71	8.98	253.40	8.44	298.80	10.13
31	87.8	210.44	6.80	209.55	6.77	275.69	8.99	261.84	8.44	308.95	10.15
32	89.6	217.25	6.81	216.33	6.77	284.68	8.99	270.28	8.44	319.10	10.16
33	91.4	224.05	6.81	223.10	6.78	293.68	9.00	278.72	8.44	329.27	10.17
34	93.2	230.86	6.81	229.88	6.78	302.68	9.00	287.15	8.44	339.46	10.18
35	95.0	237.67	6.81	236.66	6.78	311.69	9.01	295.59	8.44	349.65	10.19
36	96.8	244.48	6.81	243.43	6.78	320.70	9.02	304.02	8.43	359.86	10.21

1°C. = $\frac{9}{5}$F. 1°F. = $\frac{5}{9}$°C

(Temperature °Fahrenheit − 32) × $\frac{5}{9}$ = temperature °Centigrade.

(Temperature °Centigrade × $\frac{9}{5}$) + 32 = temperature °Fahrenheit.

Values as given are in small calories per gram molecular volume of gas (1 molecular volume = 22.4 liters at 0°C., 760 mm. of mercury pressure.)

TABLE 15.—THERMAL CAPACITY IN SMALL CALORIES PER GRAM MOLECULAR VOLUME, 0 TO 360°C., GAS AT CONSTANT PRESSURE—(*Continued*)

Temperature		O_2 CO, N_2	Dif. per °C.	H_2	Dif. per °C.	CO_2 and SO_2	Dif. per °C.	H_2O	Dif. per °C.	CH_4	Dif. per C.
°C.	°F.										
0	32	0.0	.....	0.0	.....	0.0	.....	0.0	.....	0.0	
10	50	67.8	6.78	67.5	6.75	88.3	8.83	84.5	8.45	98.4	9.84
20	68	135.7	6.79	135.1	6.76	177.2	8.89	169.0	8.45	198.0	9.96
30	86	203.6	6.80	202.8	6.77	266.7	8.95	253.4	8.44	298.8	10.08
40	104	271.7	6.81	270.6	6.78	356.8	9.01	337.8	8.44	400.8	10.20
50	122	339.9	6.82	338.4	6.79	447.5	9.07	422.1	8.43	504.0	10.32
60	140	408.2	6.83	406.4	6.80	538.8	9.13	506.3	8.43	608.4	10.44
70	158	476.6	6.84	474.4	6.80	630.7	9.19	590.6	8.42	714.0	10.56
80	176	545.0	6.85	442.5	6.81	723.1	9.25	674.7	8.42	820.8	10.68
90	194	613.6	6.86	610.8	6.82	816.2	9.30	758.9	8.41	928.8	10.80
100	212	682.3	6.87	769.1	6.83	909.8	9.36	843.0	8.41	1,038.0	10.92
110	230	751.0	6.88	747.5	6 84	1,004.0	9.42	927.0	8.41	1,148.4	11.04
120	248	820.0	6 89	816.0	6.85	1,098.7	9.47	1,011.2	8.41	1,260.0	11.16
130	266	888.9	6.90	884.6	6.86	1,194.0	9.53	1,095.2	8.41	1,372.8	11.28
140	284	958.0	6.91	953.2	6.87	1,289.9	9.59	1,179.3	8.40	1,486.8	11.40
150	302	1,027.2	6.92	1,022 0	6.88	1,386.3	9.64	1,263.3	8.40	1,602.0	11.52
160	320	1,096.5	6.93	1,090.8	6.89	1,483.3	9.70	1,347.3	8.40	1,718.4	11.64
170	338	1,165.9	6.94	1,159.8	6.89	1,580.8	9.75	1,431.4	8 40	1,836.0	11.76
180	356	1,235.3	6.95	1,228.8	6.90	1,678.9	9.81	1,515.4	8.40	1,954.8	11.88
190	374	1,304.9	6.96	1,297.9	6.91	1,777.5	9.86	1,599.5	8.41	2,074.8	12.00
200	392	1,374.6	6.97	1,367.1	6.92	1,876.7	9.92	1,683.5	8.41	2,196.0	12.12
210	410	1,444.4	6.98	1,436.4	6.93	1,976.4	9.97	1,767.6	8.41	2,318.4	12.24
220	428	1,514.3	6.99	1,505.8	6.94	2,076.6	10.02	1,851.7	8.41	2,442.0	12.36
230	446	1,584.2	7.00	1,575.3	6.95	2,177.3	10.07	1,935.9	8.41	2,566.8	12.48
240	464	1,654.3	7.01	1,644.9	6.96	2,278.6	10.13	2,020.1	8.42	2,692.8	12.60
250	482	1,724.5	7.02	1,714.6	6.97	2,380.4	10.18	2,104.3	8.42	2,820.0	12.72
260	500	1,794.8	7.03	1,784.3	6.98	2,482.7	10.23	2,188.5	8.43	2,948.4	12.84
270	518	1,865.2	7.04	1,854.1	6.98	2,585.5	10.28	2,272.8	8.43	3,078.0	12.96
280	536	1,935.6	7.05	1,924.1	6.99	2,688.8	10.33	2,357.2	8.44	3,208.8	13.08
290	554	2,006.2	7.06	1,994.1	7.00	2,792.6	10.38	2,441.6	8.44	3,340.8	13.20
300	572	2,076.9	7.07	2,064.2	7.01	2,897.0	10.43	2,526.1	8.45	3,474.0	13.32
310	590	2,147.7	7.08	2,134.4	7.02	3,001.8	10.48	2,610.6	8.45	3,608.4	13.44
320	608	2,218.6	7.09	2,204.7	7.03	3,107.1	10.53	2,695.2	8.46	3,744.0	13.56
330	626	2,289.5	7.10	2,275.1	7.04	3,212.9	10.58	2,779.9	8.47	3,880.8	13.68
340	644	2,360.6	7.11	2,345.6	7.05	3,319.2	10.63	2,864.7	8.48	4,018.8	13.80
350	662	2,431.8	7.12	2,416.1	7.06	3,426.0	10.68	2,949.5	8.48	4,158.0	13.92
360	680	2,503.0	7.13	2,486.8	7.07	3,533.2	10.73	3,034.4	8.49	4,298.4	14.04

To express the values in B.t.u's. per cubic foot at 0° C., 760 mm. mercury pressure, multiply the thermal capacity in calories by 0.00502.

To express the values in B.t.u's. per cubic foot at 60° F., 30 in. of mercury pressure (15.5 °C., 762 mm. of mercury), multiply the thermal capacity in calories by 0.00474.

TABLE 15.—THERMAL CAPACITY IN SMALL CALORIES PER GRAM MOLECULAR VOLUME, 0 TO 3000°C., GAS AT CONSTANT PRESSURE—(*Continued*)

Temperature		O_2, CO, N_2	Dif. per °C.	H_2	Dif. per °C.	CO_2 and SO_2	Dif. per °C.	H_2O	Dif. per °C.	CH_4	Dif. per °C.
°C.	°F.										
000	32	0	.....	0	.....	0	.....	0	.....	0	
100	212	682	6.82	679	6.79	909	9.09	843	8.43	1,038	10.38
200	392	1,375	6.92	1,367	6.88	1,876	9.67	1,684	8.41	2,196	11.58
300	572	2,077	7.02	2,064	6.97	2,896	10.20	2,527	8.43	3,474	12.78
400	752	2,789	7.12	2,770	7.06	3,966	10.70	3,377	8.49	4,872	13.98
500	932	3,512	7.22	3,485	7.15	5,081	11.16	4,237	8.60	6,390	15.18
600	1,112	4,244	7.32	4,209	7.24	6,239	11.58	5,112	8.76	8,028	16.38
700	1,292	4,986	7.42	4,942	7.33	7,436	11.96	6,008	8.95	9,786	17.58
800	1,472	5,738	7.52	5,685	7.42	8,667	12.31	6,927	9.20	11,664	18.78
900	1,652	6,501	7.62	6,436	7.51	9.929	12.62	7,875	9.48	13,662	19.98
1,000	1,832	7,273	7.72	7,196	7.60	11,219	12.90	8,857	9.81	15,780	21.18
1,100	2,012	8,055	7.82	7,965	7.69	12,532	13.13	9,875	10.19	18,018	22.38
1,200	2,192	8,848	7.92	8,743	7.78	13,865	13.33	10,936	10.61	20,376	23.58
1,300	2,372	9,650	8.02	9,530	7.87	15,215	13.49	12,043	11.07	22,854	24.78
1,400	2,552	10,462	8.12	10,326	7.96	16,577	13.62	13,201	11.58	25,452	25.98
1,500	2,732	11,285	8.22	11,131	8.05	17,947	13.71	14,414	12.13	28,170	27.18
1,600	2,912	12,117	8.32	11,945	8.14	19,323	13.76	15,687	12.73	31,008	28.38
1,700	3,092	12,959	8.42	12,768	8.23	20,700	13.77	17,023	13.36	33,966	29.58
1,800	3,272	13,811	8.52	13,600	8.32	22,075	13.75	18,428	14.05	37,044	30.78
1,900	3,452	14,674	8.62	14,441	8.41	23,443	13.69	19,907	14.79	40,242	31.98
2,000	3,632	15,546	8.72	15,291	.8.50	24,802	13.59	21,463	15.56	43,560	33.18
2,100	3,812	16,428	8.82	16,150	8.59	26,147	13.45	23,101	16.38		
2,200	3,992	17,321	8.92	17,015	8.68	27,475	13.28	24,826	17.25		
2,300	4,172	18,223	9.02	17,896	8.77	28,782	13.07	26,641	18.15		
2,400	4,352	19,135	9.12	18,782	8.86	30,064	12.82	28,552	19.11		
2,500	4,532	20,058	9.22	19,677	8.95	31,318	12.54	30,562	20.10		
2,600	4,712	20,990	9.32	20,581	9.04	32,539	12.22	32,676	21.14		
2,700	4,892	21,932	9.42	21,494	9.13	33,725	11.86	34,899	22.23		
2,800	5,072	22,884	9.52	22,416	9.22	34,871	11.46	37,235	23.36		
2,900	5,252	23,847	9.62	23,347	9.31	35,974	11.03	39,689	24.53		
3,000	5,432	24,819	9.72	24,287	9.40	37,030	10.56	42,264	25.75		

The values in these tables, except for methane, are based upon formulas given by Lewis and Randall, *J. Am. Chem. Soc.*, Vol. XXXIV, p. 1128, Sept., 1912.

The specific heats per gram molecular volume of gas for constant pressure and absolute temperature (T) are for,

O_2, N_2 and CO $= 6.50 + 0.0010T$
H_2 $= 6.50 + 0.0009T$
CO_2 and SO_2 $= 7.0 + 0.0071T - 0.00000186T^2$
H_2O vapor $= 8.81 - 0.0019T + 0.00000222T^2$
CH_4 $= 6.50 + 0.012T$

The values for methane are based on LeChatelier and Mallard's values as given by Damour in text on "Industrial Furnaces."

TABLE 16.—BAROMETRIC READINGS IN MILLIMETERS AND INCHES

Millimeters	Inches	Millimeters	Inches	Millimeters	Inches	Millimeters	Inches
700	27.56	723	28.47	746	29.37	769	30.28
701	0.60	724	0.50	747	0.41	770	0.32
702	0.64	725	0.54	748	0.45	771	0.36
703	0.68	726	0.58	749	0.49	772	0.39
704	0.72	727	0.63	750	0.53	773	0.43
705	0.76	728	0.66	751	0.57	774	0.47
706	0.80	729	0.70	752	0.61	775	0.51
707	0.84	730	0.74	753	0.65	776	0.55
708	0.88	731	0.78	754	0.69	777	0.59
709	0.91	732	0.82	755	0.73	778	0.63
710	0.95	733	0.86	756	0.76	779	0.67
711	0.99	734	0.90	757	0.80	780	0.71
712	28.03	735	0.94	758	0.84	781	0.75
713	0.07	736	0.98	759	0.88	782	0.79
714	0.11	737	29.02	760	0.92	783	0.83
715	0.15	738	0.06	761	0.96	784	0.87
716	0.19	739	0.10	762	30.00	785	0.91
717	0.23	740	0.13	763	0.04	786	0.94
718	0.27	741	0.17	764	0.08	787	0.98
719	0.31	742	0.21	765	0.12	788	31.02
720	0.35	743	0.25	766	0.16	789	0.06
721	0.39	744	0.29	767	0.20		
722	0.43	745	0.33	768	0.24		

TABLE 17.—CORRECTION FACTORS FOR TEMPERATURE AND PRESSURE BASED ON GAS SATURATED WITH AQUEOUS VAPOR

American Meter Company, Inc., New York

Temperature F.°	Barometer																			
	28.6	28.7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
107	.816	.820	.823	.826	.829	.832	.835	.838	.841	.844	.847	.851	.854	.857	.860	.864	.867	.870	.874	.877
106	.820	.823	.826	.829	.832	.835	.838	.841	.844	.847	.851	.854	.857	.860	.863	.867	.870	.874	.878	.881
105	.823	.827	.830	.833	.836	.839	.842	.845	.848	.851	.855	.858	.861	.864	.867	.871	.874	.878	.881	.884
104	.827	.830	.833	.836	.829	.842	.845	.848	.851	.854	.858	.861	.864	.867	.871	.874	.878	.881	.884	.887
103	.830	.834	.837	.840	.843	.847	.849	.852	.855	.858	862	.865	.868	.871	.874	.878	.881	.885	.888	.891
102	.834	.837	.840	.843	.847	.850	.853	.856	.859	.862	.865	.868	.871	.874	.878	.881	.885	.888	.891	.894
101	.837	.840	.843	.846	.850	.853	.856	.859	.862	.865	.868	.872	.875	.878	.882	.885	.888	.891	.895	.898
100	.840	.843	.846	.849	.853	.856	.859	.862	.865	.868	.872	.875	.878	.881	.885	.888	.891	.895	.898	.901
99	.844	.847	.850	.853	.857	.860	.863	.866	.869	.872	.876	.879	.882	.885	.889	.892	.895	.898	.902	.905
98	.847	.850	.853	.856	.860	.863	.866	.869	.872	.875	.879	.882	.885	.888	.892	.895	.898	.902	.905	.908
97	.850	.853	.856	.859	.863	.866	.870	.873	.876	.879	.882	.885	.888	.891	.894	.898	.901	.905	.908	.911
96	.854	.857	.860	.863	.867	.870	.873	.876	.879	.882	.886	.889	.892	.895	.898	.901	.904	.908	.911	.914
95	.857	.860	.863	.866	.870	.873	.876	.879	.882	.885	.889	.892	.895	.898	.901	.904	.908	.911	.914	.918
94	.860	.863	.866	.869	.873	.876	.879	.882	.885	.888	.892	.895	.898	.901	.904	.907	.911	.914	.918	.921
93	.863	.866	.869	.872	.876	.879	.883	.886	.889	.891	.895	.898	.901	.904	.907	.910	.914	.918	.921	.924
92	.866	.869	.872	.875	.879	.882	.885	.889	.892	.894	.898	.902	.904	.907	.910	.914	.917	.921	.924	.928
91	.869	.872	.875	.879	.882	.885	.889	.892	.895	.898	.802	.905	.908	.911	.914	.917	.921	.924	.928	.931
90	.872	.875	.878	.881	.885	.888	.892	.895	.898	.901	.905	.908	.911	.914	.917	.920	.924	.927	.931	.934
89	.875	.878	.882	.885	.889	.892	.895	.898	.901	.904	.907	.910	.914	.917	.920	.923	.927	.931	.934	.937
88	.878	.881	.885	.888	.892	.895	.898	.901	.904	.907	.910	.913	.917	.920	.923	.926	.930	.934	.937	.940
87	.881	.884	.888	.891	.895	.898	.901	.904	.907	.910	.913	.916	.920	.923	.926	.929	.933	.937	.940	.943
86	.884	.887	.890	.894	.898	.901	.904	.907	.910	.913	.916	.919	.923	.926	.929	.932	.936	.940	.943	.946
85	.887	.890	.893	.896	.900	.903	.906	.909	.913	.916	.919	.922	.926	.929	.932	.936	.939	.943	.946	.949
84	.889	.893	.896	.899	.903	.906	.909	.912	.915	.919	.922	.925	.928	.932	.935	.939	.942	.946	.949	.952
83	.892	.895	.899	.902	.906	.909	.912	.915	.918	.921	.924	.928	.931	.935	.938	.942	.945	.949	.952	.955
82	.895	.898	.901	.905	.908	.911	.914	.918	.921	.924	.927	.931	.934	.937	.941	.945	.948	.951	.954	.958
81	.898	.901	.905	.908	.911	.914	.917	.921	.924	.927	.930	.934	.937	.940	.944	.948	.951	.954	.957	.960
80	.901	.904	.907	.910	.914	.917	.920	.923	.927	.930	.933	.937	.940	.943	.946	.950	.954	.957	.960	.963
79	.904	.907	.910	.914	.917	.920	.923	.926	.930	.933	.936	.939	.943	.946	.949	.953	.956	.960	.963	.967
78	.906	.909	.913	.916	.919	.923	.926	.929	.932	.936	.939	.942	.946	.949	.952	.9 6	.959	.962	.966	.969

Temperature	77	.909	.912	.915	.919	.922	.925	.928	.931	.935	.938	.942	.945	.948	.951	.955	.958	.962	.965	.968	.972
	76	.911	.915	.918	.921	.925	.928	.931	.935	.938	.941	.944	.948	.951	.954	.958	.961	.964	.968	.971	.975
	75	.914	.917	.921	.924	.928	.931	.934	.937	.940	.943	.947	.950	.954	.957	.960	.963	.967	.971	.974	.978
	74	.917	.920	.924	.927	.930	.933	.937	.940	.943	.947	.950	.953	.957	.960	.963	.966	.970	.973	.977	.980
	73	.920	.923	.926	.930	.933	.936	.940	.943	.946	.949	.953	.956	.960	.963	.966	.969	.972	.976	.980	.983
	72	.922	.925	.929	.932	.935	.939	.942	.945	.949	.952	.955	.959	.962	.965	.968	.972	.975	.979	.982	.986
	71	.925	.928	.931	.935	.938	.941	.945	.948	.951	.954	.958	.961	.965	.968	.971	.975	.978	.981	.985	.989
	70	.927	.931	.934	.937	.941	.944	.947	.950	.954	.957	.960	.964	.967	.970	.974	.977	.980	.984	.988	.991
	69	.930	.933	.937	.940	.944	.947	.950	.953	.957	.960	.963	.967	.970	.973	.977	.980	.983	.987	.990	.994
	68	.932	.936	.939	.942	.946	.949	.952	.956	.959	.962	.966	.969	.972	.976	.979	.983	.986	.989	.993	.997
	67	.935	.938	.942	.945	.949	.952	.955	.959	.962	.965	.968	.972	.975	.979	.982	.985	.989	.992	.996	1.000
	66	.938	.941	.944	.948	.951	.954	.958	.961	.964	.968	.971	.974	.978	.981	.985	.988	.992	.995	.998	1.002
	65	.941	.944	.947	.950	.954	.957	.960	.963	.967	.970	.973	.977	.980	.984	.987	.991	.994	.997	1.001	1.005
	64	.943	.946	.949	.953	.956	.959	.963	.966	.969	.973	.976	.980	983	.986	.990	.994	.997	1.000	1.004	1.008
	63	.945	.949	.952	.955	.959	.962	.965	.969	.972	.975	.979	.982	.985	.989	.993	.996	1.000	1.003	1.006	1.010
	62	.947	.951	.954	.958	.961	.964	.968	.971	.975	.978	.981	.985	.988	.991	.995	.999	1.002	1.005	1.009	1.013
	61	.950	.954	.957	.961	.964	.967	.971	.974	.977	.981	.984	.987	.991	.994	.998	1.001	1.005	1.008	1.011	1.015
	60	.952	.956	.959	.963	.966	.969	.973	.976	.980	.983	.986	.990	.993	.997	1.000	1.004	1.007	1.010	1.014	1.017
	59	.955	.959	.962	.966	.969	.972	.976	.979	.983	.986	.989	.992	.995	.999	1.003	1.006	1.010	1.013	1.016	1.020
	58	.957	.961	.964	.968	.971	.975	.978	.981	.985	.988	.992	.995	.998	1.002	1.005	1.009	1.012	1.016	1.019	1.023
	57	.960	.963	.967	.970	.974	.977	.980	.984	.988	.991	.994	.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025
	56	.962	.966	.969	.973	.976	.979	.982	.986	.990	.993	.996	1.000	1.003	1.007	1.010	1.014	1.017	1.021	1.024	1.028
	55	.965	.968	.972	.975	.979	.982	.985	.989	.993	.996	.999	1.002	1.006	1.009	1.013	1.016	1.020	1.023	1.027	1.030
	54	.967	.970	.974	.977	.981	.984	.988	.991	.995	.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033
	53	.969	.973	.976	.980	.983	.986	.990	.993	.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.031	1.035
	52	.971	.975	.978	.982	.985	.989	.992	.996	.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038
	51	.974	.977	.981	.984	.988	.991	.995	.998	1.002	1.005	1.009	1.012	1.016	1.019	1.023	1.026	1.030	1.033	1.037	1.040
	50	.976	.980	.983	.987	.990	.994	.997	1.001	1.004	1.008	1.011	1.015	1.018	1.022	1.025	1.029	1.032	1.036	1.039	1.043
	49	.979	.982	.986	.989	.993	.996	1.000	1.003	1.007	1.010	1.014	1.017	1.021	1.024	1.028	1.031	1.035	1.038	1.042	1.045
	48	.981	.985	.988	.992	.995	.999	1.002	1.006	1.009	1.013	1.016	1.020	1.023	1.027	1.030	1.034	1.037	1.041	1.044	1.048
	47	.984	.987	.991	.994	.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033	1.036	1.040	1.043	1.047	1.050
	46	.986	.990	.993	.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.032	1.035	1.039	1.042	1.046	1.049	1.053
	45	.989	.992	.996	.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038	1.041	1.045	1.048	1.052	1.056
	44	.991	.994	.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033	1.036	1.040	1.043	1.047	1.050	1.054	1.058
	43	.993	.997	1.001	1.004	1.008	1.011	1.015	1.018	1.022	1.025	1.029	1.032	1.036	1.039	1.043	1.046	1.050	1.053	1.057	1.060
	42	.995	.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038	1.041	1.045	1.048	1.052	1.055	1.059	1.063
	41	.998	1.001	1.005	1.009	1.012	1.016	1.019	1.023	1.026	1.030	1.034	1.037	1.041	1.044	1.048	1.051	1.055	1.058	1.062	1.065
	40	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.032	1.036	1.039	1.043	1.046	1.050	1.053	1.057	1.060	1.064	1.068
	39	1.002	1.006	1.010	1.013	1.017	1.020	1.024	1.028	1.031	1.035	1.038	1.042	1.045	1.049	1.052	1.056	1.059	1.063	1.066	1.070

Observed volume multiplied by factor corresponding to observed temperature and barometric pressure equals corrected volume.

TABLE 18.—REDUCTION OF BAROMETER READINGS TO STANDARD TEMPERATURE

Brass scale

The table gives the correction for the barometer reading in inches and the temperature in degrees Fahrenheit for a brass scale graduated to be correct at 62° F. The correction is to be subtracted.

Temp. ° F.	Observed height in inches								
	27.0	27.5	28.0	28.5	29.0	29.5	30.0	30.5	31.0
32	0.009	0.009	0.009	0.009	0.009	0.009	0.010	0.010	0.010
34	.013	.014	.014	.014	.014	.015	.015	.015	.015
36	.018	.019	.019	.019	.020	.020	.020	.021	.021
38	.023	.024	.024	.025	.025	.025	.026	.026	.027
40	.028	.029	.029	.030	.030	.031	.031	.032	.032
42	.033	.034	.034	.035	.035	.036	.038	.037	.038
44	.038	.039	.039	.040	.041	.041	.042	.043	.044
46	.043	.044	.044	.045	.046	.047	.048	.048	.049
48	.048	.049	.050	.050	.051	.052	.053	.054	.055
50	.053	.054	.055	.055	.057	.058	.058	.059	.060
52	.058	.059	.060	.060	.062	.063	.064	.065	.066
54	.062	.063	.065	.066	.067	.068	.069	.071	.072
56	.067	.068	.070	.071	.072	.074	.075	.076	.077
58	.072	.073	.075	.076	.078	.079	.080	.082	.083
60	.077	.078	.080	.081	.083	.084	.086	.087	.089
62	.082	.083	.085	.086	.088	.090	.091	.093	.094
64	.087	.088	.090	.092	.093	.095	.097	.098	.100
66	.092	.093	.095	.097	.099	.100	.102	.104	.105
68	.097	.098	.100	.102	.104	.106	.107	.109	.111
70	.102	.103	.105	.107	.109	.111	.113	.115	.117
72	.107	.108	.110	.112	.114	.116	.118	.120	.122
74	.111	.113	.116	.117	.120	.122	.124	.126	.128
76	.116	.118	.121	.123	.125	.127	.129	.131	.133
78	.121	.123	.126	.128	.130	.132	.135	.137	.139
80	.126	.128	.131	.133	.135	.138	.140	.142	.145
82	.131	.133	.136	.138	.141	.143	.146	.148	.150
84	.136	.138	.141	.143	.146	.148	.151	.153	.156
86	.141	.143	.146	.148	.151	.154	.156	.159	.162
88	.146	.148	.151	.154	.156	.159	.162	.165	.167
90	.151	.153	.156	.159	.162	.165	.167	.170	.173
92	.156	.158	.161	.164	.167	.170	.173	.176	.178
94	.160	.163	.166	.170	.172	.175	.178	.181	.184
96	.165	.168	.171	.174	.178	.181	.184	.187	.190
98	.170	.173	.177	.179	.183	.186	.189	.192	.195

TABLE 19.—CORRECTION FOR CAPILLARY DEPRESSION OF MERCURY IN A GLASS TUBE

Correction to be added

Diam. of tube	Height of meniscus in centimeters							
	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18
0.4	0.083	0.122	0.154	0.198	0.237			
0.5	.047	.065	.086	.119	.145	0.180		
0.6	.027	.041	.056	.078	.098	.121	0.143	
0.7	.018	.028	.040	.053	.067	.082	.097	.113
0.8	....	.020	.029	.038	.046	.056	.065	0.077
0.9	....	0.015	0.021	0.028	0.033	0.040	0.046	0.052
1.0	....	....	.015	.020	.025	.029	.033	.037
1.1	....	....	.010	.014	.018	.021	.024	.027
1.2	....	....	.007	.010	.013	.015	.018	.019
1.3	....	....	.004	.007	.010	.012	.013	.014

Table 20.—Use of the Common Indicators

Substance titrated	Methyl orange	Phenolphthalein	Other indicators
Acetic acid	Useless.	Good.	
Citric acid	Useless.	Good.	
Oxalic acid	Useless.	Good.	Litmus is good.
Phosphoric acid	Good. Changes at NaH_2PO_4.	End at Na_2HPO_4, but indistinct.	Cochineal is good with change at Na_2HPO_4.
HCl, HNO_3, H_2SO_4	Good.	Good.	
Ammonia	Good.	Useless.	Cochineal and methyl red are good.
Na_2CO_3, K_2CO_3	Good. Changes at 2NaCl and 2KCl.	End at $NaHCO_3$, but not sharp.	Cochineal is good.
Bicarbonates	Good.	Useless.	Cochineal is good.
Sulfurous acid	Good. Changes at $NaHSO_3$.		
NaOH, KOH, $Ba(OH)_2$, $Ca(OH)_2$.	Good.	Good.	
Borates	Good. Not affected by H_3BO_3.	Useless.	Lacmoid is good.
Alkali metal silicates		Good. Not affected by H_2SiO_4.	
Cyanides	Good.		
Amines	Good		Methyl red is good.
Pyridine	Useless.		Methyl red is good.
Picric acid	Usless.		Methyl red is good.
MoO_3, WO_3	Good. Changes at Na_2MoO_4, etc.		
	Is, in general, a good indicator for strong acids and strong bases and weak bases, but is useless for weak acids. Color is red in acid and yellow in alkalies. Must be used cold.	Is, in general, a good indicator for strong acids and strong bases and weak acids, but is useless for weak bases. CO_2 must be absent at the end. Color is red in alkaline and colorless in acid solutions.	

Standard solutions used for titrating are assumed to be HCl and NaOH.

TABLE 21.—MEASURES AND WEIGHTS

Measures of capacity

A. Dry Measure

1 bushel = 2150.42 cubic inches.
1 bushel = the volume of 77.627 pounds of distilled water at 4°C.
Legal: 1 liter = 0.908 quart.
1 bushel = 4 pecks = 8 gallons = 32 quarts = 35.24229 liters.
1 peck = 2 gallons = 8 quarts = 8.81057 liters.
1 gallon = 4 quarts = 4.40528 liters.
1 quart = 1.10132 liters.

B. Liquid Measure

1 U. S. gallon = 231 cubic inches.
1 gallon = the volume of 8.3388822 pounds = 58378 troy grains of distilled water at 4°C. (Stillman, "Engineering Chemistry.")
1 gallon = 58318 grains of water at 62°F. (U. S. Phar.)
1 gallon = 58334.9+ grains of pure water at 60°F., weighed in air at 60°F., at barometric pressure of 30 inches of mercury. (Mason)
Legal: 1 liter = 1.0567 quart = 0.26417 gallon.
1 gallon = 4 quarts = 8 pints = 32 gills = 3.78544 liters.
1 quart = 2 pints = 8 gills = 0.94636 liter.
1 pint = 4 gills = 0.47318 liter.
1 gill = 0.118295 liter.
1 cubic foot = 7.48 gallons = 28.315 liters = 62.42 pounds of water at 60°F. (Stillman.)
1 cubic foot of water at 62°F. = 62.355 pounds avoirdupois = 28320 grams.
1 cubic inch of water at 62°F. = 0.0361 pounds avoirdupois = 16.387 grams. (Watts' Dictionary, V, 1010.)

Linear Measure

1 yard = 0.91440 meter.
1 foot = 0.30480 meter.
1 inch = 0.0254 meter.
39.37 inches = 1 meter.

WEIGHTS

1 grain troy = 0.0648004 gram.
1 pound troy = 0.822857 pounds avoirdupois.
1 pound avoirdupois = 7000 grains troy = 1.215279 pounds troy.

Troy Weight

1 pound = 12 oz. = 240 pwts. = 5760 grains = 373.2418 grams.
1 oz. = 20 pwts. = 480 grains = 31.1035 grams.
1 pwt. = 24 grains = 1.5552 grams.
1 grain = 0.0648 grams.
1 gram = 15.432 troy grains.

Avoirdupois Weight

1 ton = 20 hundredweight = 2240 pounds = 1016.04 kilograms.
1 hundredweight = 112 pounds = 50.80 kilograms.
1 pound = 16 ounces = 256 drams = 7000.00 grains = 453.5900 grams.
1 ounce = 16 drams = 437.50 grains = 28.3495 grams.
1 dram = 27.34 grains = 1.7718 grams.
1 net ton = 2000 pounds = 29166$\frac{2}{3}$ ozs. troy = 907.19 kilograms.

Metric Ton

1 metric ton = 1000 kilograms.

CONVERSION OF THERMOMETER READINGS

To convert Fahrenheit to Centigrade, subtract 32 and multiply by $\frac{5}{9}$.
To convert Centigrade to Fahrenheit, multiply by $\frac{9}{5}$ and add 32.

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