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QUANTITATIVE ANALYSIS

Methods of
Separation and Measurement

QUANTITATIVE ANALYSIS

Methods of Separation and Measurement

M. G. MELLON

Professor of Analytical Chemistry
Purdue University

New York – 1956

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PREFACE

During each passing year the author's experience as a teacher has further strengthened his belief that the over-all problem of quantitative analysis has two phases. The first phase, chiefly or entirely chemical, involves whatever is necessary in the way of treatment of the sample, separation of the desired constituent, and conversion of that constituent (or its chemical equivalent) into measurable form. The second phase, entirely physical, involves measurement of this desired constituent (or its chemical equivalent).

The sequence of operations that make up these two phases, being that actually followed in applied analysis, logically determines the organization of Part One, "General Principles." Thus, selection and preparation, measurement, and preliminary treatment of the sample are discussed first. Then follow chapters on various methods of separating and measuring the desired constituent. This basic organization is further emphasized in the laboratory exercises in Part Two, where each procedure follows the same sequence of operations.

Although measurement of the desired constituent is the ultimate and inevitable objective in every procedure, each operation in the sequence is a unit in itself. For example, precipitation is a separative process that may equally well precede gravimetric, titrimetric, or colorimetric measurement of the constituent so separated. Conversely, any one of the four general methods of separation discussed in this book may be used prior to a gravimetric measurement. Therefore, each operation receives separate treatment in Part One. Moreover, the discussion of principles is segregated from the specific laboratory exercises to emphasize that the theory of each method is independent of any particular sequence in which it may be applied. Cross references appear both in the general discussions to applications and in the exercises to discussions of relevant principles.

In the inevitable choice between comprehensive treatment of a few

types of methods and less thorough treatment of many types of methods the author has selected the latter alternative in the belief that detailed consideration of theoretical topics properly belongs in a study of physical chemistry. In addition, because the segregation of inorganic from organic chemistry seems unnecessary (and largely undesirable) to the analyst, who must deal with the chemistry of all elements and their compounds, the methods presented in this book are sufficiently general to include all elements of the Periodic Table. This broad coverage has particular value for the many students who now devote only one semester to quantitative analysis, since this brief period constitutes their sole opportunity to gain some perspective of the variety and applications of the many methods in everyday use.

At the same time some detail with regard to at least one subject is desirable from a psychological standpoint; little depth of understanding can be expected from the student if a course consists largely of gadget-punching excursions past expensive and impressive, but little-understood, instruments. The author has therefore concentrated on titrimetry, having selected this method as the most feasible means of teaching a number of generally important items, such as sampling, weighing, chemical transformations, keeping records, precision, accuracy, and care in working.

All numerical problems have been grouped together in Part Three in order that suggestions for solving the various types may be given coordinate treatment. Specific applications in the laboratory exercises are indicated by cross references. Calculative work is considered very important in the author's testing program, since a student who cannot calculate his results shows little understanding of what he has done.

A library problem is included to illustrate the use of analytical literature, a valuable tool that is too often overlooked in undergraduate courses. Examination of many new graduate students, from all parts of the country, has revealed widespread lack of familiarity with the general problem of devising a method for a new situation.

The author desires to express his obligation to many writers for facts and ideas and to various publishers and manufacturers for permission to include specific items. The primary objective in writing the book has been to utilize all such material to present a perspective of the place and method of contemporary quantitative analysis.

Acknowledgment of special indebtedness is made to a former colleague, Dr. P. J. Elving, and to two present colleagues, Drs. Thomas De Vries and W. W. Brandt, who read the entire manuscript and made many valuable suggestions. The further assistance of Drs. De Vries and Brandt in reading proofs is also deeply appreciated.

M. G. MELLON

Lafayette, Indiana
March, 1955

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CHAPTER 1

INTRODUCTION

Modern chemical technology and chemical research operate largely on the basis of data resulting from tests and analyses of materials. These data serve for the evaluation of raw materials, processes, and products. The engineering specifications and test methods of the American Society for Testing Materials,[1] for example, exceed 9,700 pages in the edition of 1952. Annual supplements, and a complete revision every three years, keep this work up to date. Agricultural, pharmaceutical, public health, and other organizations have comparable, smaller compilations.

The concern of these official organizations, as well as of individuals, for such information may be indicated by the following questions, illustrative of hundreds that arise daily: Down to what temperature is an automobile engine protected by ethylene glycol solution in the radiator? Does the ocean contain enough gold to justify recovery of the metal? Is a given water chlorinator operating to provide the residual chlorine necessary to make the water supply safe for human use? What should one pay per ton for a uranium ore, if the price per pound is quoted in terms of the content of uranium oxide in the ore? Will a given source of supply of sand meet the purity specifications for making optical glass?

The answers to these questions, and to others like them, depend on information provided by quantitative analytical data. Obviously, then, as an area of study quantitative analysis has great practical importance. Before proceeding to an examination of the technical details of quantitative analysis, the student should have a general idea of what the subject includes and of its importance to mankind, both as a practical science and as a more broad educational discipline.

[1] Often abbreviated as ASTM.

THE NATURE AND FUNCTION OF QUANTITATIVE ANALYSIS

In order to understand the nature of quantitative analysis, the student must have some comprehension of its position in the general field of chemical knowledge.

Subject Matter

Chemistry may be defined as the physical science which deals with the nature, structure, and properties of the substances of our world. Because chemistry, as so defined, covers a vast field of knowledge, some subdivision of that knowledge is necessary. Various systems of classification, differing with the classifier and the purpose of the system, have been developed. The 33 divisions used in *Chemical Abstracts* illustrate one useful system. This scheme includes, as do others, a division known as **analytical chemistry,** which deals with the methods of ascertaining the constituent parts of substances.

The word "analysis" was introduced by Robert Boyle to denote the determination of the composition of substances. According to an official report, "analysis is the separation, the identification, or the determination of the concentration of part or all of the constituents or components of a sample." [2] A somewhat broader interpretation considers analytical chemistry as "including all technics and methods for obtaining information regarding the composition, identity, purity, and constitution of samples of matter in terms of the kind, quantity, and groupings of atoms and molecules, as well as the determination of those physical properties and behavior which can be correlated with these objectives." [3] If one accepts the latter concept, analytical chemistry includes not only methods for securing knowledge of the elemental composition of materials, but also the way atoms are put together to form molecular units in these materials. The determination of organic functional groups is therefore included.

One of the two subdivisions of analytical chemistry, **qualitative analysis,** includes methods and technics for determining the identity and nature of constituents of a given sample; the other subdivision, **quantitative analysis,** includes methods and technics for determining the amounts of these constituents. The present book is devoted to quantitative methods.

Other terms widely used in analytical chemistry, with which the student should be familiar, follow.[4]

Determination is the act, process, or result of any measurement.

[2] Ashley *et al., Anal. Chem.* **24,** 1348 (1952).
[3] Elving, *Anal. Chem.* **22,** 962 (1950).
[4] See Ashley, *op. cit.*

Method is a definite or orderly manner, way, or mode of doing anything.

Procedure is a series of steps in the conduct of an experiment.

Process is a series of actions or operations, especially when directed to a definite end.

Practical Importance

The practical value of quantitative chemical analysis to the student of chemistry, to chemical research, to chemical industry, and to the general public has already been mentioned. The importance of the quantitative analytical method, and of data derived from application of the method, to each of these groups, will be outlined briefly.

Trade and production. One of the largest of our chemical industries published an advertisement stating that "as unto the bow, the cord is; so is accurate chemical analysis to the production of pure, uniform products. It is the rudder to all chemical progress." In general, it may be stated that the making, selling, buying, and using of chemical products are dependent on analytical control.

Basic raw materials (ores, coal, limestone, milk, and wheat, for example) are purchased on the basis of tests and analyses, rather than on the claims of salesmen. The chief analyst may be the final signer of a contract, indicating thereby his approval of the specifications of the material in question.

The questions of the suitability of a given substance for a specific purpose, and, if it is suitable, the amount to be used, often depend upon the chemical composition of the substance. Thus, a steel mill may divide its incoming cars of coal into two lots on the basis of the sulfur content. Only low-sulfur coal is satisfactory for metallurgical furnaces; high-sulfur coal serves for steam generation.

Manufacturing processes for such products as iron and steel, sulfuric acid, dyes, and cement, in which chemical composition affects significantly

TABLE 1.1

ANALYTICAL DETERMINATIONS FOR SELECTED PRODUCTS

Material	*Tonnage*	*Elements*	*Number of Determinations*
Aluminum and alloys	1,000,000	42 elements	12,000,000
Pig iron	50,000,000	C, Mn, P, S, Si	2,000,000
Steel, open hearth	82,000,000	C, Mn, P, S, Si	27,000,000
Steel, electric	5,000,000	Cr, Mo, Ni, V, W, C, Mn, P, S, Si	35,000,000

the quality or nature of the product, are controlled by analyses. The volume of analytical data for several metallurgical products in a prewar year of operation is shown in Table 1.1.

Manufactured products are tested to determine whether or not they meet specifications. Chemicals of the best grade bear labels showing the maximum amounts of impurities present. Below is a facsimile of such a label, for the analytical data only, of potassium dichromate "Analytical Reagent" grade.[5]

$K_2Cr_2O_7$ F. W. 294.21

MEETS A. C. S. SPECIFICATIONS

Maximum Limits of Impurities

Aluminum (Al)	0.002%
Calcium (Ca)	0.001%
Chloride (Cl)	0.001%
Insoluble Matter and NH_4OH Ppt.	0.010%
Sodium (Na)	0.02 %
Sulfate (SO_4)	0.005%

ASSAY ($K_2Cr_2O_7$)..... 99.95–100.05%

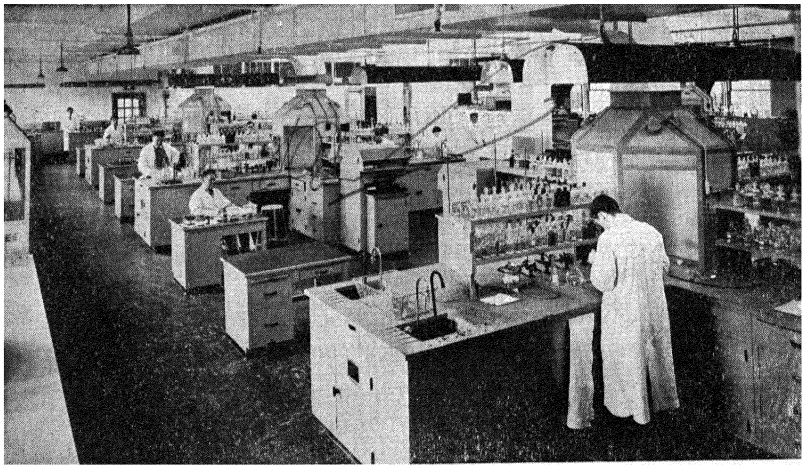


Figure 1.1

View of an analytical laboratory (courtesy Merck and Co.).

Figure 1.1 is a view of a modern laboratory where such analytical work is done. The measuring instruments are usually kept in a separate

[5] Reproduced through courtesy of Mallinckrodt Chemical Works.

part of the laboratory as a protection against chemical action likely to occur in the preparative area of the laboratory.

Research and development. In his *History of Chemistry* Meyer states, "The history of analytical chemistry is placed first in order since it is an indispensable aid to all chemical research." In chemical industry research workers rely constantly upon analytical data to guide them in their work. In fact, analytical chemistry functions primarily as a measuring stick, serving to indicate what is being used, what is happening, and what is being obtained.

Figure 1.2 illustrates the relationship of chemical analysis to both production and research.

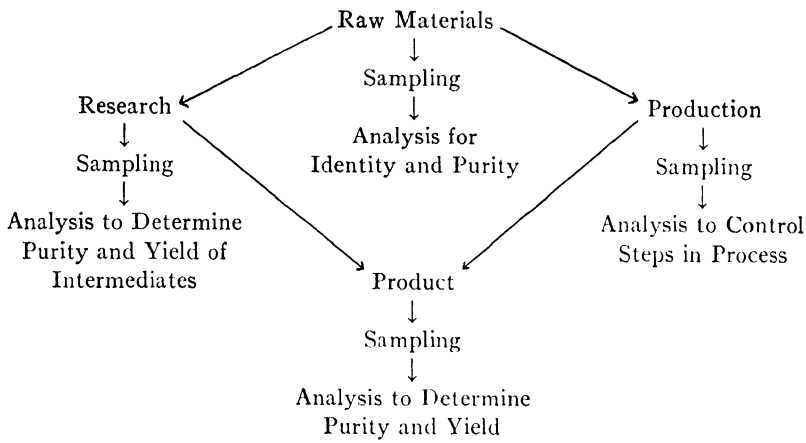


Figure 1.2

Role of sampling and analysis in the processing of materials and in research.

Public welfare. Chemical analysis is equally important in work which affects the public welfare. Federal, state, and municipal laboratories use this method in research and in testing materials that are controlled by food and fertilizer laws and general public health regulations involving sanitation. The proper administration and enforcement of laws pertaining to foods, drugs, air, water, sewage, and many other items is dependent on accurate chemical analysis.

The United States government and all progressive chemical concerns buy products on the basis of specifications and analyses. If ultimate consumers were in a position to follow this practice in purchasing products, the benefits to them would undoubtedly be enormous. In recent

years many department stores and mail-order houses have established testing divisions for the examination of goods.

Educational Values

Many students consider quantitative analysis a kind of "meat and potatoes" training, because it is, usually, the first course in their study of chemistry that seems to offer immediate possibilities for application. However, the student who has had thorough training in analytical chemistry may acquire not only information for practical use, but, in addition, a permanent body of knowledge and skills that may be designated as "educational."

There is bound to be some acquisition of facts in the study of chemical analysis. The amount will depend to some extent upon the nature of the course and the way it is taught. To a greater extent it will depend on the student's own efforts, for education is ultimately a personal problem. Reference works are available for the serious student to read. To be of most value, such reading should be done with the objective of maintaining a broad perspective of the subject.

One of the important reasons for the study of quantitative analysis is that many students majoring in nonchemical fields, for example, metallurgical engineering or medicine, will be called upon in their future professional activities to decide whether or not chemical analyses are necessary and to interpret analytical data as guides for making recommendations. It is doubtful that an individual who has not actually performed analyses has any real appreciation of such points as the methods of making determinations, evaluation of information supplied by the data obtained, the analyst's problems, and what can reasonably be expected of analysts.

In addition to the more or less direct educational benefits described above, the study of quantitative analysis provides certain others, designated by Frost[6] as "by-product" values:

1. Stimulation of the logical mental processes.
2. Training of the memory in the technic of the art.
3. Practice in learning how to work effectively.
4. Cultivation of self-reliance and resourcefulness.
5. Development of neatness and care.
6. Education in dependability and integrity.
7. Encouragement in the use of the scientific method.
8. Development of admiration and respect for nature and natural laws.

[6] *Science* **58**, 256 (1923).

METHODOLOGY OF QUANTITATIVE ANALYSIS

In order that the student may have a general perspective of material to be covered in an introductory study of quantitative chemical analysis, a brief survey of the subject is presented at this point. The main purpose of the remainder of the book is to develop this outline in detail.

The general problem of making a chemical analysis quantitatively involves a determination of one or more constituents in a given sample of material. This determination is accomplished by measurement, directly or indirectly, of some property of the desired constituent, often after some form of separation or purification. Quantitative analysis, then, involves primarily a study of methods employed in handling the sample and the desired constituent.

The Sample

The first requirement for a chemical analysis is a sample of the material to be analyzed. The general operations usually performed as steps in an analysis are selection and preparation, measurement, and treatment.

The analyst must select his sample and then subject it to whatever preparation is needed to make the collection of reliable analytical data possible. The preparation necessary varies, depending principally on the nature of the material sampled and on its physical state.

With the exception of a few technics, such as refractometry, quantitative manipulation of a sample necessitates that the sample be measured. The operation of measurement is usually accomplished by a determination of the mass or volume of the material.

In many cases one may proceed with the analysis as soon as the sample is measured, no preliminary treatment of the material being required. More frequently, however, certain transformations in the original material are necessary to subsequent operations. Some of the treatments more or less commonly employed are concentration, fusion, dissolution, and adjustment of such conditions as acidity, state of oxidation, or degree of complexation.

The Desired Constituent

The next concern of the analyst is to ascertain what fraction of the sample consists of the constituent sought. In some cases substances are of such a nature that, after preparing and treating the sample as necessary, the analyst may proceed at once with the determination.

More often, however, he must separate the desired constituent from interfering constituents before its amount can be determined. Therefore, there are often two parts to the problem of determining the desired constituent: separation and actual measurement.

In quantitative separations the desired constituent, either by itself or in association with other substances, is isolated. Isolation involves removal from the system of either the desired constituent or the interfering constituent(s). Methods of separation most commonly used include volatilization, precipitation, electrodeposition, and partition.

After making any necessary separation(s), the analyst proceeds to the next and final general operation—ascertaining the amount(s) of the desired constituent(s) present. Two general kinds of methods of measurement may be used.

Where the desired constituent can be suitably isolated, the measurement of *some property of this constituent,* or of *something chemically related to this constituent,* makes possible a determination of the amount of the constituent. The properties most suitable for such measurement are mass, volume, pressure, and heat of reaction.

For a large group of constituents that cannot be thus isolated, or need not be, the determination depends finally upon the measurement of *some property of a system containing the desired constituent.* Some of the more useful methods applicable to this group are based on the measurement of the absorption of radiant energy (e.g., colorimetry), specific gravity, freezing and boiling points, and phase equilibration.

An Example of the "Why" and the "How" of an Analysis

To supplement the preceding discussion of general purposes and procedures of chemical analysis, the purpose of a specific analysis will now be considered and one method of performing the analysis described briefly.

When an individual who has no chemical training reads in his daily paper that the Mesabi Range in Minnesota is being worked out, and that, consequently, our supply of high-grade iron ore is nearing depletion, he does not, in all probability, stop to reflect what the expression "high-grade" iron ore means. Nor, when he reads that the low-grade ore of Labrador is being investigated as a prospective source of supply of iron, does he consider how the fact that one ore is high-grade and the other low-grade was determined. He may assume that a high-grade ore is one that contains much iron, whereas a low-grade ore is one containing little iron. From this assumption he may arrive at the vague conclusion that it would be more economical to recover iron from an ore containing much of the metal than from one containing little. If

he were a student of analytical chemistry, however, he would know that iron ore is graded as a result of chemical analysis, and that the potential economic value of iron ore deposits may be calculated from data so derived.

As the first operation in his analysis of an iron ore, the analyst obtains a sample suitable for analysis. This sample must be representative of the deposit concerning which he wants information, for his problem is to determine the average iron content of the total deposit.

The sample is then weighed and treated to isolate the iron present in it. One method of isolating the iron, at least in readily soluble ores, is to precipitate it as an insoluble compound under conditions such that other substances in the ore remain in solution. The ore is dissolved in a suitable acid. Ammonium hydroxide is then added until the solution is faintly alkaline, at which point hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$, precipitates. This precipitate is filtered, and the mother liquor and any other materials clinging to the precipitate removed by washing with water. Finally, the residue of hydrated iron oxide is heated to a high temperature and weighed as ferric oxide, Fe_2O_3.

Having determined the weights of the sample and of the iron oxide obtained therefrom, and knowing that each gram-mole of ferric oxide contains two gram-atoms of iron, the analyst can calculate the percentage of the iron in the ore. Numerically, his calculation is

$$\% \text{ Fe} = \frac{\text{weight of } Fe_2O_3 \times \dfrac{2 \times 55.85}{159.7}}{\text{weight of sample}} \times 100$$

Examination of this procedure to determine the amount of iron in a sample of ore reveals four well-defined stages: (1) a representative sample was secured and measured; (2) the desired constituent, iron, was isolated in a form that could be measured; (3) the desired constituent, following conversion to ferric oxide, was weighed; and (4) the amount of iron in the sample was calculated. The final data of the analysis are interpreted as indicating a low- or high-grade ore.

Examination of the various types of analytical procedures described in this book, and of others used in actual chemical practice, discloses that many methods consist essentially of such operative stages, with either fewer or more procedural steps.

CHAPTER 2

SELECTION AND PREPARATION

THEORY

Before the theory of sampling is considered, the term "sampling" must be defined. Briefly, the sample is the actual material (1) upon which some measurement is made directly, or (2) from which portions are taken for preparation of a system that is susceptible to measurement in order to determine the amount of a desired constituent. In either case, the basic requirement of the analytical sample is that it represent accurately the entire material for which an analysis is desired. An auxiliary requirement of the sample is that its complete history be known, to insure that the basic requirement is met. All the operations involved in getting this sample, then, are known as sampling.

Polycomponent materials vary in composition from strictly homogeneous distribution of the components to maximum heterogeneity in this respect. Homogeneous materials present no problem, of course, provided only that an adequate amount of the sample is available. In contrast, sampling of heterogeneous materials may be so difficult that this operation is the most exacting part of the whole process of analysis.

Heterogeneous materials are usually sampled with one of two objectives in mind. One of these objectives is analysis of a specific portion of the heterogeneous material at particular locations. The analyst may wish to study the corrosion products on contact points in automatic telephone switchboards, for example, or to determine the progress of self-purification of water in a river by analyzing samples at stated distances below the sewer outlet into that river. Obviously, his samples for each of these analyses must be representative, not of the whole material but only of that portion to be tested. Such specially selected portions are sometimes called "specimens."

The other objective is analysis of the total heterogeneous material by determination of the chemical composition of a sample of that material.

Since only a small amount of that material is actually used in most ordinary analytical determinations, it is essential that this sample have the same average composition as the large mass of heterogeneous material from which it was obtained.

The magnitude of the problem of sampling heterogeneous material is illustrated by the standard method for determination of the calorific value of coal. The procedure specifies that a carload of some 50 tons of coal be reduced to a 1-g sample (that is, from 45,000,000 g to 1 g). This sample is then burned in a calorimeter. The precision, or reproducibility, of the sampling process is evidenced by the fact that the allowance for different determinations by the standards of the American Society for Testing Materials is 0.3 per cent for the same laboratory and 0.5 per cent for different laboratories.

The importance of sampling in chemical analysis can hardly be overemphasized. The prospective purchaser of a mineral deposit, for example, may send a representative many miles to make certain that the sample is properly taken. In certain legal cases, an accurate knowledge of the complete history of the sample usually is required to sustain the validity of the evidence.

Not only is careful analysis of a nonrepresentative sample a total waste of time, materials, and effort, but the analytical data obtained may be misleading and may, therefore, result in an erroneous or even harmful interpretation of the nature of the sample analyzed. In spite of the obvious significance for successful analysis of precise sampling, the analyst very often has no part in securing the sample; it is simply delivered to him, and he must assume that it is reliable. If, as a result of ignorance, carelessness, or intentional misrepresentation, a nonrepresentative sample has been chosen for analysis, nothing the analyst can do will compensate for the error.

Standardized procedures for sampling, as well as for testing and analyzing, the more important classes of natural and manufactured products have been issued by governmental bureaus, testing associations, and industrial groups. Some of these organizations are the Federal Specifications Board, the United States Bureau of Mines, the American Society for Testing Materials, the American Petroleum Institute, the Association of Official Agricultural Chemists, the American Pharmaceutical Association, and the American Public Health Association. The sampling procedures have been standardized on the basis of data obtained from experimental study, statistical theory, and long practice. Usually the operational details comprise the opening section of such official methods of analysis.

TECHNIC

Commercial consulting and analytical laboratories with a general practice conduct analyses of a great variety of materials—from the contents of the stomach of a poisoned cow to the emanations of pitchblende ores. Discussion of technic here, however, will be limited to the general problems involved in selecting and preparing samples, as they apply to gases, liquids, and solids. Special treatises should be consulted for information on specific industrial and natural products.[1]

Selection of the Sample

The first problem that arises in the selection of a sample pertains to the amount of that sample available for analysis. If the atmosphere is to be analyzed for neon, the amount of sample is unlimited. If, however, the material to be analyzed must be preserved in its essential form for further service (e.g., a special ignition point), the amount of sample available is subject to restriction. For a carload of coal, for example, 1 per cent of the total load (1000 lbs, for a 50-ton car) is recommended as the proper amount of gross sample to be used for analysis. (Reference is made later to the problem of selecting a 1-g working sample.)

For different materials in different physical states, a variety of methods is used to obtain samples; in general, these methods may be classified as *manual* and *mechanical*. The former method, in which the material is sampled in some way by hand, has always been widely used and is still employed in the great majority of analyses. The mechanical method may be considered as one division of automatic methods of analysis. If the analytical method is entirely automatic, removal of a sample from the material may not be necessary, the procedure being one which produces a continuous record of the composition of the material as it passes the sampling mechanism.

There are three main technics for obtaining samples: continuous, intermittent, and "grab." In *continuous sampling*, a definite fraction of the material to be analyzed is continuously diverted from the material as it moves along a conveyer of some sort; e.g., through a slot in a loading chute 1 per cent of a carload of coal may be removed to form the gross sample. In *intermittent sampling*, every *n*th unit of the material is set aside to form the gross sample; thus, every hundredth sack or shovelful of ore may be tossed aside. *Grab sampling*, which involves taking random samples, is usually restricted to homogeneous materials; if it is

[1] See Furman, *Scott's Standard Methods of Chemical Analysis*, Vol. II, sec. 1, Van Nostrand, 1939.

used for heterogeneous materials, a large number of grab samples are taken in an appropriate distribution throughout the material. Specific application of the general processes of sampling to gases, liquids, and solids will now be considered.

Gases. Material in the gaseous state presents a peculiar problem in that the substance is invisible in most instances. Thus, the analyst who attempts to obtain a representative sample of air has no visible evidence from which to decide whether or not the atmosphere has, at any given time, been well mixed by air currents. Therefore, in handling air with the usual type of gas buret, he may draw in the sample and expel it several times in order to secure a portion reasonably representative of the whole at the given location.

General gas analysis (e.g., determination of inert gases of the atmosphere, fluorine in volcanic gases, gases dissolved in metals, and radioactive emanations) involves many special sampling problems. For details, the student may refer to publications that deal specifically with the methods of gas analysis.[2]

Liquids. If material in the liquid state is available in reasonable amount, the analyst has, as a rule, no difficulty in selecting a reliable sample, especially if the whole mass can be stirred to insure thorough mixing. Some liquids, however, do present sampling problems; in biochemical work, for example, some body fluid may be both scarce and instable when isolated. Representative samples of large bodies of liquids that cannot be stirred must be secured by mixing portions selected at different locations and from different depths.

The analyst may not wish to have an average sample for the entire liquid system. As mentioned previously, he may test the natural purification of a river contaminated with sewage by taking samples at a number of places downstream from the sewer outlet. Again, he may determine the most favorable location for a plant for extracting bromine from sea water by taking samples of water from a number of places.

In various situations mechanical or automatic methods are readily adaptable to the sampling of both gases and liquids.

Solids. Substances in the solid state present a number of sampling problems. The material available may vary in size from a mountain range to a portion so small that a microbalance is necessary to weigh it. Again, the material may be relatively uniform in composition, as in an

[2] Altieri, *Gas Analysis and Testing of Gaseous Materials,* American Gas Assn., 1945; Dennis and Nichols, *Gas Analysis,* Macmillan, 1929; Lunge-Ambler, *Technical Gas Analysis,* Van Nostrand, 1934; Parr, *The Analysis of Fuel, Gas, Water, and Lubricants,* McGraw-Hill, 1932; Universal Oil Products Co., *U.O.P. Laboratory Test Methods for Petroleum and Its Products,* 1947.

alloy free from segregation; or the constituents may be very unevenly distributed, as in a gold ore.

The steps in sampling heterogeneous solids are (1) collection of the gross sample, (2) reduction of the gross sample to a size suitable for transportation from the site of sampling to the laboratory, and (3) preparation of the sample for analysis. The gross sample usually consists of several "sampling units" where this unit is the smallest portion of material containing, to a high degree of probability, the same proportions of different-sized particles as the original mass of material. In most cases, the "sampling unit" will be 500 times the weight of one of the largest particles in the material being sampled. In order to keep the total weight of the gross sample within feasible limits, reduction in size of the largest particles may be necessary.

The wide variety of solids encountered makes necessary a number of methods for taking suitable samples. The sampling of several typical commercial materials will now be described, to illustrate something of the way in which sampling is handled in individual cases.

Metals and alloys known to be free of segregation need only to be filed, drilled, milled, turned, or cut in small pieces if they are in thin sheets or wire. For a material in which the components are not uniformly distributed, a procedure found satisfactory consists in taking fine drillings from as many locations as necessary in order to secure a fair sample when the drillings are all mixed together. Samples taken in this way (from certain cast irons, for example) may not yield very consistent results in repeated analyses. The composition of the finely divided drillings often has been found to differ considerably from that of the coarser particles.

In a case-hardened steel, the composition of the "case" differs from that of the remaining material. The sample taken depends upon whether the analyst wants the thin exterior layer or the interior part.

As a sampling method for a carload of coal being unloaded by hand, a shovelful of coal may be thrown aside at definite intervals—say one in every 100. If the material is not too coarse, a split shovel, designed for this purpose, may be used. Powdered material on a conveyer can be sampled automatically by means of a small cup dipped periodically into the coal stream. This same process is applicable to finely crushed ore moving on a conveyer or in a chute.

With rocks, ore veins, and similar materials, a sufficient number of individual samples must be secured from different locations to insure the representative character of the composite sample. The same precaution must be taken in soil sampling. In the last-mentioned case, a special

problem may arise if the sample is representative only of material at certain depths. Soil augers or borers are used to take the portion desired. Other kinds of special samplers may also be used.

A carload of grain may be sampled by the employment of a hollow tube, called a "sampling thief." Such a tube has openings of varying sizes along its length. The "thief" is inserted in a systematic way into the grain, at various locations in the car, and a series of samples is thus obtained. These samples, when composited (mixed together), give a gross sample representative of the load of grain as a unit.

Preparation of the Sample

Samples of gases, liquids, and homogeneous solids generally need no treatment to prepare them, if the material was carefully selected. It is necessary only to preserve the amount required for the tests and analyses to be made. Homogeneous solids may require subdivision prior to analysis.

Nonhomogeneous solids present various problems in preparation of the sample so that it will yield reliable analytical data. Broadly speaking, the preparative treatment includes subdivision and mixing. The more specific preparations and the methods for accomplishing them will be discussed briefly. Although the statements in the discussion that follows are generally applicable, many modifications may be made, of course, in adapting the operations to samples containing constituents with different properties.

Chemical changes. The first problem with some samples (for example, coal) is to get them through the preparative operations without the occurrence of changes in their composition. A change in chemical composition of the sample will, of course, produce a corresponding change in the relative proportions of the constituents present. Such changes may be classified roughly as reaction of the sample with something in its environment and decomposition of the sample. In being subject to these changes, solids are unique only to the extent that the changes may be occasioned by the treatment used in preparing the sample.

Common constituents found in the atmosphere that are likely to affect certain samples include oxygen, carbon dioxide, and water vapor. Thus, ferrous salts will oxidize, sodium hydroxide will absorb carbon dioxide, and various compounds will deliquesce or hydrolyze in presence of moisture. The loss of water of crystallization through efflorescence is an example of decomposition of the sample. The analytical effect of loss of hygroscopic moisture by drying is the same, of course.

In the examination of many natural and synthetic products it is often

desirable or necessary that the analyst handle the analytical samples under conditions whereby the moisture content of the sample is in equilibrium with the water content of the atmosphere.

Moisture in samples such as wet coal necessitate the taking of special precautions, for as much as 10 to 15 per cent of water may be encountered. If 1 per cent of an ordinary carload of coal is selected, this gross sample will be approximately 1000 lbs. of wet material of uneven size and composition. The problem, then, is to secure 1 g of homogeneous sample. The mass is too wet to grind, and even if it were not, moisture would be lost in the process. A prerequisite to extensive subdivision is drying, which may be accomplished by "air drying" or by desiccation under specified conditions. The ASTM methods[3] for analysis of wet coal require that the gross sample be crushed, as rapidly as possible, finely enough to pass through a 4-mesh sieve, from which a relatively large portion (15 lbs.) is then taken. Samples of 500 g are then spread out in weighed pans to dry. When the loss in weight is not over 0.1 per cent per hour, the sample is considered to be in equilibrium with the atmosphere and the percentage of moisture is calculated as the loss on air-drying.

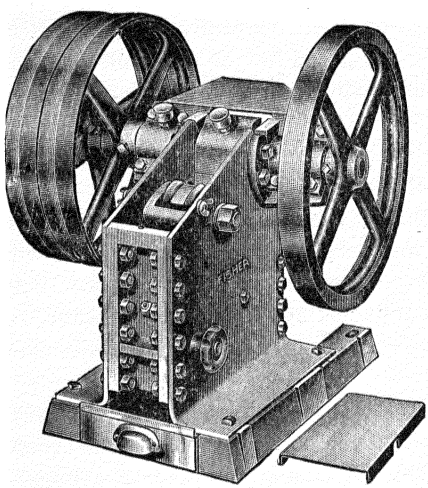


Figure 2.1

Braun type of power-operated crusher (courtesy Fisher Scientific Co.).

Subdivision. In earlier years, thousands upon thousands of samples were reduced by hand, from the original massive pieces to particles small enough to give reliable analytical results. Since general use of such laborious methods is no longer made, unless absolutely necessary, the present discussion of subdivision of samples is confined chiefly to methods employing various types of power equipment.

When the bulk of the material selected is in relatively large pieces, crushing is the first step in the process of securing small size particles. For different materials different types of crushers seem to work best.

Figure 2.1 illustrates a power-operated type of jaw crusher for rocks,

[3] ASTM Designations D 492-48, "Sampling Coals," and D 271-48, "Sampling and Analysis of Coal and Coke," in *ASTM Standards 1952,* Part 5, pp. 799, 807.

ores, and other hard materials. This crusher will reduce 2-in. rock to pieces ¼ in. or smaller in size. The crushing is accomplished between a movable and an adjustable jaw. An eccentric imparts a circular movement to the upper end of the movable jaw, while a toggle compels the lower end to describe an arc of a small circle. The combined movement is forward and downward, crushing and impelling the discharge. The stationary jaw may be closely adjusted by a knob on the front of the machine, or it may be removed entirely for cleaning.

Similar results can be secured with powerful gyratory and roller crushers. The rolls in the latter type can be equipped with a scraper to remove solids that tend to stick, a difficulty not so easily remedied in the jaw-type of machine.

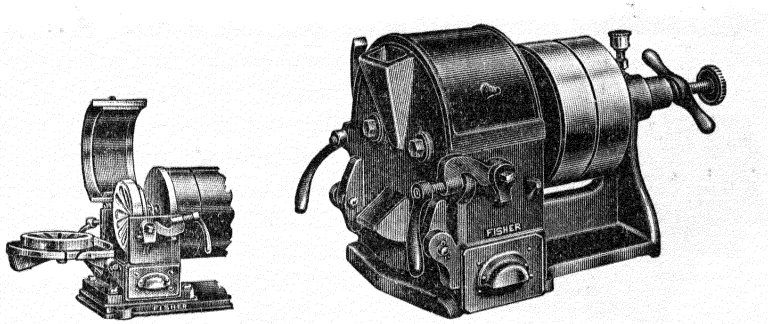


Figure 2.2

Pulverizer open (left) and closed (right) (courtesy Fisher Scientific Co.).

The crushing process yields a product, some of the particles of which are sufficiently fine for analysis; this is especially true for samples of low crushing strength, such as coals and some limestones. In most cases, however, the subdividing process must be continued by means of some type of grinding. The analyst's traditional grinding apparatus has always been a mortar and pestle. This device is not used so frequently today unless some hard sample, such as a silicate rock, must be brought down to 200-mesh size in an agate mortar. Even then a mechanically operated mortar is available. Three common mechanical devices for reducing materials to particles small enough to pass through a 60- or 100-mesh sieve are rotary grinders, ball mills, and rod mills.

Figure 2.2 illustrates a grinder or pulverizer in which a vertical convex disk turns against a stationary concave plate. An adjusting screw provides for setting of the distance between the grinding plates to produce

the desired degree of fineness. This type of machine is very effective in reducing material such as dry limestone to 100-mesh size. Samples carrying much moisture cannot be handled in either crushers or grinders. Official methods for testing coal, for example, direct that a portion of the gross sample be air-dried under specified conditions to obtain the moisture so evolved. The air-dry coal may then be ground in pulverizers like that shown in Figure 2.2. Samples for another moisture determination are removed when the material reaches 20-mesh size. Grinding is then resumed until the mass passes a 60-mesh screen.

Ball or rod mills are used extensively for still finer grinding. Mills made of porcelain with flint balls are convenient for preparing samples for analysis. The grinding process is very slow with substances as hard as granite, but many limestones and metallic ores grind quite satisfactorily. Small rod mills rotated in the same way are more effective for hard samples, as the force of impact of the heavy steel rods on the particles is much greater. Rod mills are usually not as convenient to clean as ball mills. The ball mill illustrated in Figure 2.3 has a capacity of 4 liters and is rotated at a speed of about 70 rev./min. Dry samples with volumes of about 1500 ml are rotated with ⅓ this volume of flint or porcelain balls ¾ to 1 in. in diameter. Before grinding samples such as those listed in the Appendix, the materials should be thoroughly dried by heating at 100 to 110°C.[4] Even then some substances give trouble by sticking to the wall of the jar.

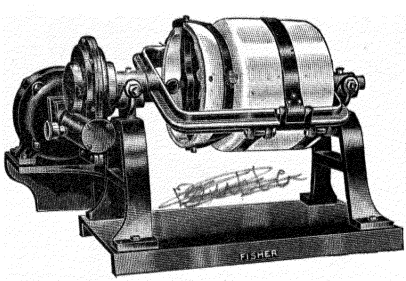


Figure 2.3

Ball mill, power operated (courtesy Fisher Scientific Co.).

Sieving. In most cases it is desirable to grind samples until they are fine enough to pass a sieve having 80 to 100 meshes per linear inch, unless objectionable chemical changes are produced thereby. To facilitate fusion, a silicate rock sample should pass a 200-mesh sieve.

Screening sieves are obtainable in sets, common mesh sizes being 4, 8, 10, 20, 35, 60, 80, 100, 150 and 200. Table 2.1 contains data for a more extensive standard series. The United States Series is based on Number 18 in the series, which has openings of 1 mm. The other series is based on the 200-mesh size, which has openings of 0.074 mm (0.0029 in.). The

[4] As the centigrade temperature scale is used throughout this book, with only two or three exceptions, the abbreviation will not be repeated.

second column in Table 2.1 shows the Rittinger geometric series, having a ratio of $\sqrt{2}$, or 1.414, between the series of opening between successive screens. The third column shows the Richards geometric series, having a ratio of $\sqrt[4]{2}$, or 1.189, between the sizes of opening between successive screens. The latter series is more closely graded than the Rittinger scale. It may be noted that the United States Series number and the mesh opening do not agree throughout the series.

TABLE 2.1

SCALE DATA FOR STANDARD SCREEN SIEVES*

	Openings (in. $\sqrt{2}$ Ratio (1.414)	*Openings* (in. $\sqrt[4]{2}$ Ratio (1.189)	*Diameter of Wire* (in.)	*U.S. Series Equivalents* Micron Designation	*U.S. Series Equivalents* Number
Mesh					
4	0.185	0.185	0.065	4760	4
5		0.156	0.044	4000	5
6	0.131	0.131	0.036	3360	6
7		0.110	0.0328	2830	7
8	0.093	0.093	0.0320	2380	8
9		0.078	0.0330	2000	10
10	0.065	0.065	0.0350	1680	12
12		0.055	0.0280	1410	14
14	0.046	0.046	0.0250	1190	16
16		0.0390	0.0235	1000	18
20	0.0328	0.0328	0.0172	840	20
24		0.0276	0.0141	710	25
28	0.0232	0.0232	0.0125	590	30
32		0.0195	0.0118	500	35
35	0.0164	0.0164	0.0122	420	40
42		0.0138	0.0100	350	45
48	0.0116	0.0116	0.0092	297	50
60		0.0097	0.0070	250	60
65	0.0082	0.0082	0.0072	210	70
80		0.0069	0.0056	177	80
100	0.0058	0.0058	0.0042	149	100
115		0.0049	0.0038	125	120
150	0.0041	0.0041	0.0026	105	140
170		0.0035	0.0024	88	170
200	0.0029	0.0029	0.0021	74	200
250		0.0024	0.0016	62	230
270	0.0021	0.0021	0.0016	53	270
325		0.0017	0.0014	44	325
400	0.0015	0.0015	0.0010	37	400

* Adapted from catalogue of W. S. Tyler Co. See also ASTM Designation E 11-39, "Standard Specifications for Sieves," in *ASTM Standards 1952*, Part 5, p. 1211.

If much screening is necessary, labor may be saved by having the set of screens mounted in a shaking device. A standard U.S. No. 40 sieve, 8 in. in diameter, is illustrated in Figure 2.4. In use, the screen is rotated to bring all fine material in contact with the wire. Only dry samples can be screened in this way. Particles sticking in the openings should never be forced through. After use, the sieve should be turned upside down and brushed or rubbed lightly to dislodge any particles caught in the meshes. Sieves should always be cleaned to prevent any possible reaction between the sample and the wire, and so that they will be ready for the next screening.



Figure 2.4

Wire-cloth screen (courtesy Fisher Scientific Co.).

Intermixing. Samples ground in ball or rod mills are likely to have the finer and coarser particles uniformly distributed. Those ground by hand or crushed in some way will probably not be sufficiently mixed. Solids may be mixed very conveniently by rotation in a ball mill. Certain materials that tend to stick on the unglazed surface of porcelain mills and balls may be handled in large glass reagent bottles, with glass marbles for balls.

Often the ground sample is mixed by hand on a piece of glazed paper of sufficient size. One corner of the paper is lifted enough to cause the material to move well toward the opposite corner. Then this opposite corner is lifted to cause the material to roll back toward the first corner. The other two corners are handled in the same way. This process of "tabling" is repeated until the mixing is completed and the material is in a cone-shaped pile in the center of the paper.

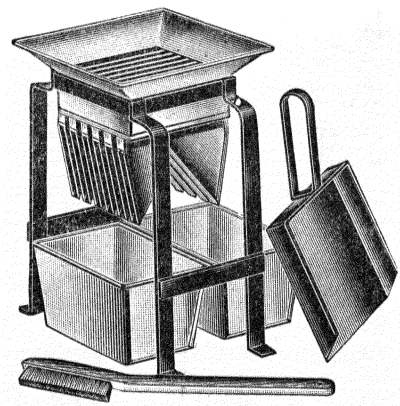


Figure 2.5

Riffle sampler (courtesy Fisher Scientific Co.).

The amount of sample thus prepared is generally much greater than is needed for the determinations in which it is to be used. The sample may be reduced to the amount desired by quartering the cone of prepared material as follows: By means of a large spatula the pile is divided in half and each half is

then split into two equal portions. Opposite quarters are removed from the paper and the two remaining are again thoroughly mixed. The quartering process is repeated as many times as necessary to bring the working sample down to the desired size. Quartering can be accomplished more easily and rapidly by means of a riffle, a mechanical device for halving the sample automatically. Figure 2.5 illustrates such a riffle sampler. The material is put into the top of the riffle with the scoop; half of the particles pass through into one sample pan and the other half go into the other pan. One pan may then be set aside and the process repeated as many times as desired. This process is a part-mechanization of the older quartering procedure.

Storage. Storage of stable samples (solid, liquid, or gaseous) presents no special problem. Insofar as possible, precautions should be taken to prevent changes in instable materials, at least until the desired analytical determinations have been made. Generally, such changes are attributable to one or more of a few types of reaction. Moist caustic soda may react with soft glass containers; radiant energy, particularly ultraviolet, will affect photochemically sensitive material; water may be lost through efflorescence or evaporation; laboratory fumes, carbon dioxide, oxygen, or water vapor may bring about certain reactions. These and other possibilities must be kept in mind. Jars of dark glass, with well-fitting closures, suffice for the storage of most samples.

CHAPTER 3

MEASUREMENT BY MASS

Many items of equipment are used by analysts dealing with a variety of industrial materials, but the equal-arm analytical balance is probably the most nearly indispensable.[1] More than a century ago Nicholson wrote that "every precise operation begins and ends with the balance." According to Guzman, gravimetry (measurement by mass) was in use in the sixteenth century.[2]

In view of the importance of this piece of apparatus, the present chapter is devoted to some of the more significant points relating to the construction and use of balances. The discussion of use applies to weighing not only of samples but also of any products derived therefrom (see Chapter 16).

First of all, the distinction between *mass* and *weight* should be noted. Weight is a measure of the force or pull of gravity on a given body. It is proportional to the mass of the body. Mass is the amount of material in a body, and it is measured by the force required to change the motion of the body. Mass is commonly measured by weighing, that is, by comparing the pull of gravity on the body, the mass of which is to be determined, with that on a standard of known mass. The value obtained by the process is often called the "weight" of the body, but, strictly speaking, it is a measure of the pull of gravity on the body. The pull of gravity on a body varies with the altitude as well as with the mass. The equal-arm balance is a weighing instrument that is independent of the numerical value of the force of gravity, since the pull is equal on both pans. With this balance it is possible actually to measure mass and not weight. However, since at any given altitude mass and weight are proportional, analysts generally use the term "weight" rather than "mass."

[1] See Oesper, *J. Chem. Educ.* 17, 312 (1940), for an account of some famous balances.
[2] *Anales soc. españ. fís. quím.* 34, 495 (1936).

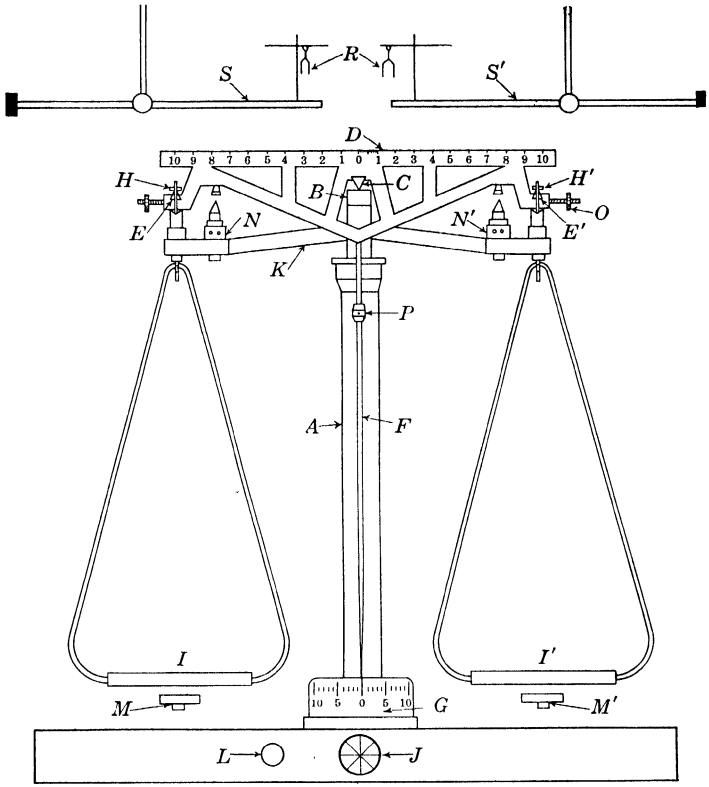


Figure 3.1

The central supporting post *A*, fastened rigidly to the base of the case, carries on its top a plane agate (synthetic sapphire is also used in newer instruments) bearing *B*, on which rests the center knife-edge agate bearing *C* of the beam *D*. The knife-edge bearings *E*, *E'*, at the ends of the beam, have the edges turned upward. The three knife-edge bearings are set so that their edges are parallel and in the same plane. The beam itself, made of some light corrosion-resistant alloy, is constructed according to one of several truss designs. Either the beam itself, or a bar fastened to it, is graduated in terms of milligrams and fractions thereof. Preferably, these marks should extend in both directions from the center, so that weighing may be done on either pan.

Most instruments have a long, slim pointer *F*, extending from the center of the beam to near the base of the case, where a graduated scale, *G*, is located to serve as a reference point when the pointer swings on release of the beam arrest. The graduations on some pointer scales start with zero on the left and extend across, with the highest value on the right. In some cases no numerals appear on the scale.

The distance from the center knife-edge to either end knife-edge is known as the *arm length*. The ratio of one arm length to the other is the *arm ratio*. Ideally, the arm ratio should be unity.

(*Caption continued at foot of following page.*)

The conventional form of balance consists of a beam supported in the center. Near each end, at points equidistant from the center fulcrum, a pan is suspended. One pan serves to hold the object to be weighed, and the other to hold the weights. All ordinarily sensitive instruments of this type are capable of detecting differences of mass of 0.1 to 0.05 mg. Micro and ultramicro balances can detect still smaller differences.

Figure 3.1 illustrates the important parts to be found on most simple analytical balances. Wood has been much used for cases, but metal is now popular. Three or four screw feet (not shown in Figure 3.1) are provided for leveling the case. Some form of bubble level or a plumb bob, in the center of the case and at the back, serves to show when the case is level.

TYPES OF BALANCES

The type of instrument described above is an ordinary balance, that is, one of conventional design. Except for improvements in materials,

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The stirrups H, H' from which the pans I, I' are suspended, have a plane agate bearing resting on the knife-edge E, E'. The upper of the two hooks on each stirrup is used for suspending the pan. The other is for suspending objects that cannot be placed directly upon the pan, or for certain special purposes, such as the use of a specific gravity plummet (see page 310). The pans and hangers are generally metal. On some balances the pan itself is interchangeable with a metal or glass part shaped like a watch glass with a handle, to be used for weighing samples. The pans and stirrups are marked in some manner to show on which end of the beam each belongs.

On all the more sensitive balances will be found some type of support for the beam and for the pans. These may be actuated by a single control device operated by turning a knob J, located in the center and at the front of the case. On many instruments this central knob operates only the beam-arresting device K. A small knob L, to the left of center, operates the pan supports M, M'. The two knobs may be concentric. The chief purpose of the pan supports is to touch the bottom of the pans just enough to keep them from swinging sidewise when the beam arrest is released. The beam rest serves both to stop the moving system and to separate slightly the knife-edge and plane agate bearings when the balance is not in use. Centering pins keep the movable parts aligned.

Finally, all analytical balances not otherwise equipped have a rider carrier S, S' for placing the piece of wire R, known as a "rider," upon the beam and for removing it again. This rider, placed on the graduated portion of the beam, provides for determination of the third and fourth decimal places in weighing. Many of the cheaper balances have only one rider, with the beam graduations extending from the center to the right-hand end. Occasionally the zero graduation mark is over the left-hand knife-edge, with the highest number, usually 10, over the right-hand knife-edge. With the beam graduated in both directions from the center, as shown in Figure 3.1, two riders provide for flexibility in weighing.

Use of the means of adjustment N, N', O, O', and P is explained under the discussion of adjustment.

beam design, and general workmanship, many modern balances do not differ essentially from those of the time of Berzelius (c. 1820). These three improvements, however, are responsible for the vast difference in the capabilities of instruments from the two different periods.

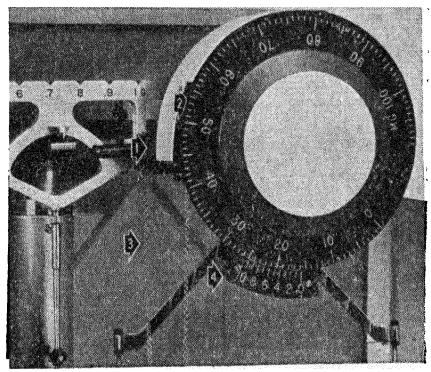
During the last few decades a number of innovations have been made on balances. In general, these changes make the operation of weighing more convenient, more rapid, and, in some cases, more precise. Some of these quick-weighing instruments are mentioned below.

Chain Balances

Probably the most striking change in balance construction was the introduction of the so-called "chainomatic" instrument. In order to weigh to four decimal places with a conventional balance, one must use fractional weights (<1 g) for the first and second places on all instruments. In addition, a 0.0050-g piece is needed for balances having less than ten major (milligram) divisions on the beam. The rider then provides for the third and fourth decimal places. Figure 3.2 illustrates the chainomatic mechanism used by one manufacturer.

Because it eliminates the necessity for handling small weights and the rider, and enables the operator to make the final adjustment with-

Figure 3.2



Chain, dial, and vernier of a chainomatic balance. On chainomatic balances one end of a small-link chain is fastened to the right of the center of the beam. The point of attachment is shown at (*1*). The other end of the chain is arranged to move in a manner to vary the length of the loop (*3*), and hence the mass, suspended from the beam. For the balance shown, the chain is wound up on a drum behind the graduated 100-mg scale (*2*). The notches shown in the beam are for a 1-g weight handled by a special carrier. For any given position (except 1 g), the numerals indicate the value in the first decimal place in grams. The method of obtaining the reading for the second, third, and fourth decimal places is illustrated by reference to the scale reading in the figure shown. The first digits of the major subdivisions (10, 20, . . .) are the values for the second decimal places; the minor subdivisions are the values for the third decimal places; and the digits 0 to 10 on the vernier scale (*4*) are the values for the fourth decimal places. The actual reading shown in the figure is 15.7 mg, or 0.0157 g. The "7" value is taken to be the nearest match point of the vernier and milligram scales (courtesy Christian Becker, Inc.).

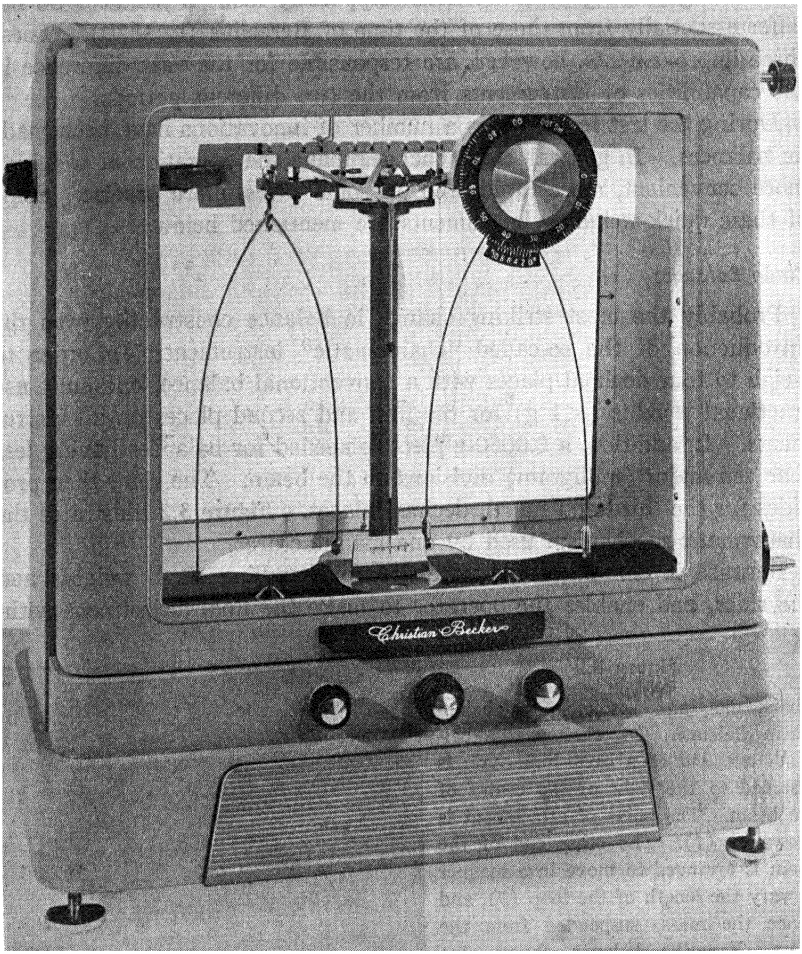


Figure 3.3

Chainomatic, magnetically damped balance (courtesy Christian Becker, Inc.).

out stopping the swinging of the beam for each change in weights, the chainomatic balance permits rapid weighing.

Figure 3.3 shows a general view of this type of balance. In another variation of the chain device the chain reel is connected to a speedometer-type of counter on which can be read directly the digits of the second, third, and fourth decimal places.

Multiple Rider Balances

The introduction of several types of multiple-rider and keyboard balances, like that illustrated in Figure 3.4, has added to the speed and convenience of weighing. These instruments have special arrangements of riders or small weights which eliminate handling of the ordinary fractional pieces. In a few instruments such mechanical devices have been extended to handle all the large weights. Because the older type

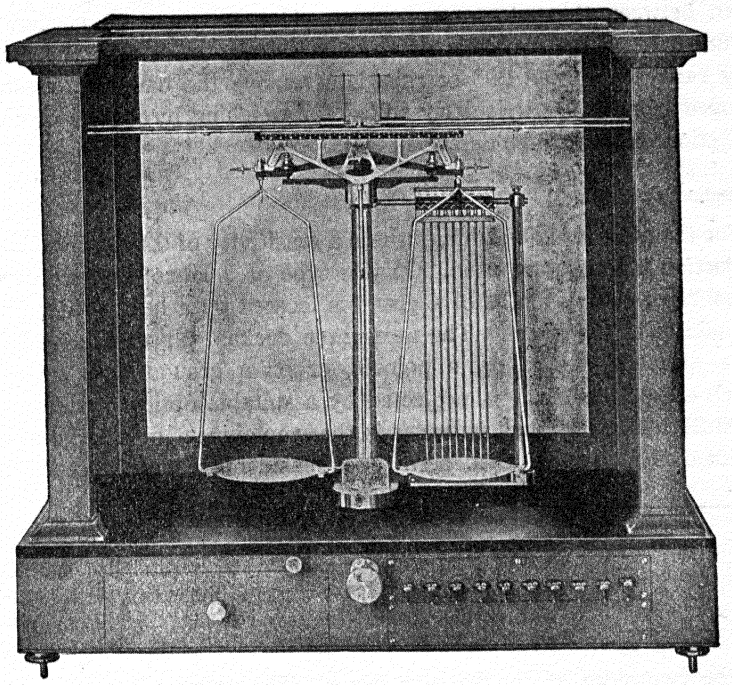


Figure 3.4

Keyboard, multiple-rider balance (courtesy William Ainsworth and Sons).

of rider is still necessary on these balances, they may be used for weighings in the usual manner in which the multiple riders are unnecessary. Such weighing cannot be done on chainomatic balances because they lack beam graduations and rider.

Damped Balances

The use of damping devices attached to balances represents another important innovation. In instruments so equipped the pointer, instead

of swinging freely back and forth, swings directly to the point of rest. The direction of swing depends upon the equilibrium adjustment. This damping of the swing is accomplished by means of air chambers or a magnetic device.

The magnetic device is simplest and cheapest. It consists, usually, either of an aluminum plate suspended from the right-hand stirrup or of aluminum plates fastened to one or each end of the balance beam so that the movement of the aluminum plate, as the beam swings, is up and down between the poles of a magnet. One arrangement is shown in Figure 3.3. Some magnetic dampers are designed so that the magnet may easily be turned 90° or raised to remove the damping effect. A damped balance is particularly suited for weighing by a type of single-deflection method, to be described later.

Projection Balances

For the most rapid weighing, where a sensitivity of 0.1 mg is adequate, projection balances are used. In this type of balance the first decimal place, representing tenths of a gram, is located by a heavy rider placed in notches in the beam. The next three decimal places are read on a scale attached to the beam pointer, or on a ground-glass screen on which the pointer scale is projected by a suitable optical system. The essential feature of such balances is the employment of a large amount of magnetic damping that permits a considerable unbalance of mass

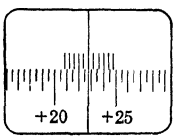


Figure 3.5

View of glass screen showing center vertical line indicating a reading of +0.0228 g; the tenths of milligrams are read directly on the vernier (courtesy Christian Becker, Inc.).

on the two sides of the balance beam. The matte glass screen of a typical projection balance is shown in Figure 3.5. Since the scale is graduated to 100 mg on each side of the center zero, the weight adjustment by the rider need be made only to the nearest tenth of a gram above or below the weight of the object being weighed. To achieve reliable values under widely different loads, such a balance must have nearly constant sensitivity (see discussion of theory, page 32).

The latest type of projection balance is designed to insure constant sensitivity. This result is achieved by having the balance loaded to capacity (200 g) at all times. The weights are counterbalanced by metal on the other end of the beam. The balance has only one pan and two knife-edge bearings. To weigh an object, the operator must

remove weights to an amount equal to the mass of the object being weighed. The weights for units and the first decimal place are determined by the turning of knobs on the front of the case. Separate dials show the mass values for the tens, units, and first decimal. Then the second, third, and fourth decimal places are indicated by an optical scale projected on a glass near the knobs. Very rapid weighing is possible with this type of balance.

Other Improvements

Some of the other improvements that have proved more or less useful are as follows: (1) a movable pointer scale, or an equilibrium-adjusting chain, either of which enables the operator easily to keep the zero point at the center of the pointer scale; (2) a reflected light beam as a substitute for the pointer, thus making possible the use of a pointer scale much longer than the ordinary scale; (3) a variable-sensitivity device making possible a preliminary selection of weights with the balance set for rapid weighing and the final adjustment of the rider with the balance set for high sensitivity; and (4) several types of vernier devices, in addition to those described.

Balances of Different Capacities

Most ordinary analytical balances are constructed for maximum loads of 200 g on each pan, and they can be read to 0.1 mg or, in instruments of the highest sensitivity, to 0.05 mg. For weighing very heavy or very light objects many special capacity balances have been made. Instruments are available for weighing objects as heavy as 5 kg. For weighing very light objects assay balances, designed usually for a maximum load of 5 g, have long been in use, chiefly in metallurgical analysis for weighing the very small "buttons" of metal obtained from gold and silver ores. Microbalances are a more recent development. The best of them are sensitive to 0.001 mg and have a maximum capacity of about 20 g. They are for analyses made on a micro scale. Their utility is increasing steadily. Even more sensitive is the quartz fiber balance used extensively in ultramicroanalysis of the transuranium elements.[3]

THEORY

Different writers have treated, in more or less mathematical detail, various items connected with the design and functioning of analytical balances. An example is Fales'[4] discussion of the justification for the

[3] Seaborg, *Chem. Eng. News* **24**, 1196 (1946).
[4] *Inorganic Quantitative Analysis*, Chapter 5, Century, 1925.

method used in calculating the zero point (see page 386), the factors affecting the time of swing, and the conditions upon which the sensitivity depends. Discussion here will be limited to a brief presentation of the subject of sensitivity.

Sensitivity may be defined, in general, as the quality of a balance which enables it to indicate slight changes in mass. Sensitivity may be expressed in several ways. Balance manufacturers usually use the term to refer to the fraction of a milligram which will change the zero point ¼ of a division of the pointer scale under full load. Such a sensitivity rating is usually 1/20 mg for high quality conventional balances. Analysts use the term in one of two ways: (1) as the number of scale divisions the zero point is displaced by a load of 1 mg, or (2) as the fraction of a milligram (in tenths) necessary to produce a displacement of one scale division. One of these values is the reciprocal of the other. The most sensitive balance will be either the one with the greatest displacement for a given load, or the one requiring the least load to produce a given displacement.

A number of factors affect the sensitivity of a balance. Their relationship may be stated mathematically by the equation

$$\tan \alpha = \frac{L}{DM} k$$

in which α = the angle through which the pointer moves, D = the distance of the center of gravity below the central knife-edge, L = length of the beam, M = mass of the beam, and k = a constant for the coefficient of friction of the given system. Because the angle α is small, the sensitivity is probably defined best as the number of scale divisions the zero point is displaced by a load of 1 mg. The equation given above shows that, in order to increase sensitivity, one or more of the following changes must be made: (1) the beam must be longer, (2) the beam must be lighter, and (3) the distance between the central plane agate bearing and the center of gravity must be smaller.

Evidently the design of a generally useful balance necessitates a compromise on these items. Minimum mass, for example, cannot be achieved with long beams. The center of gravity cannot be raised indefinitely if the instrument is to be stable. Modern balances have relatively light aluminum alloy beams, but the construction must be heavy enough so that they will remain rigid when supporting the maximum load for which the instrument is designed.

With increasing load on a balance, an increase in friction on the bearings may reasonably be expected and a slight bending of the beam.

These factors lead to different sensitivities for different loads. The maximum load on a balance should not exceed an amount sufficient to reduce the sensitivity below 40 per cent of its value for no load. As a criterion for judging the safe load for a given balance, a curve which co-ordinates sensitivity and load is desirable. The construction of such a curve is described on page 389.

USE OF BALANCES

Location

In general, the analytical balance should be located where it may be used as conveniently and efficiently as possible.[5] The first requirement in selecting a location is that the support for the balance must be such as to permit obtaining satisfactory results with the instrument. Because of vibration, such results are not always easy to achieve in some industrial laboratories and in poorly constructed academic buildings. To minimize vibration, sponge rubber may often be used advantageously in the arrangement of a usable support. Many arrangements for the vibration-free support of balances, including micro balances, have been described.[6]

Direct exposure of the balance to sunlight should be avoided. Uneven illumination may change the arm ratio, and hence the zero point, by heating the beam unequally.

Most analytical chemists believe that an instrument as sensitive as a balance should not be kept in a laboratory where corrosive fumes are likely to come in contact with the metal parts. Consequently, balances are usually placed in separate balance rooms. With the increasing effectiveness of ventilating systems in modern laboratories, however, there is a growing tendency to abandon the separate balance room, and place the balance nearer the working place of the individual using it. Some balances have double cases for protection.

Cleanliness

Balances that have just been unpacked must be brushed out with a camel's hair brush and the working parts wiped carefully with a clean cloth. A corner of the cloth may be moistened with ethanol for wiping the agate bearings.

The inside of the balance case should be kept scrupulously clean at

[5] See MacNevin, "The Analytical Balance, Its Care and Use," Handbook Publishers; "The Care and Use of Analytical Balances," The Torsion Balance Co.; and "Use and Care of Analytical, Micro, and Semimicro Ainsworth Balances," Wm. Ainsworth and Sons.

[6] Kirner, *Ind. Eng. Chem., Anal. Ed.* **9**, 300 (1937); Steyermark, *Ind. Eng. Chem., Anal. Ed.* **17**, 523 (1945).

all times, both to avoid contamination of materials being weighed and to avoid injury to the delicate parts of the balance mechanism. When chemicals are accidentally spilled on the balance pan or case floor, they should immediately be removed with a camel's hair brush or by other suitable means.

Testing and Adjustment

There are several methods for adjustment of analytical balances. The operator should understand the common methods for testing his instrument and the means provided for effecting such adjustments as an intelligent analyst can make. With the balance located in the position where it is to be used, the instrument should be examined to determine whether its adjustment is such as to permit weighings to be made with the desired accuracy. Simple methods of testing a balance for correct adjustment may be found in the literature.[7] Tests for conformity to specifications for government purchase are of interest.[8]

Level of the case. The level bulb or plumb bob should be inspected to determine whether the case is level. Any necessary adjustment may be made by turning one or more of the screw feet.

Pan rests. With the beam arrested, the pan rests should just touch the bottom of the pans, so that lateral swinging may be stopped. Where the supporting mechanism is externally controlled, the relative position of the two arms may be varied by means of an adjusting screw. In internally controlled instruments with a single dual-release knob, the operator may have to open the operating mechanism underneath the base to make any adjustments.

Beam rest. When the beam rest is raised into position, the beam, and stirrups should be lifted just enough to keep the agate knife-edge and plane bearings from making contact with each other. Small adjusting screws (N, N' in Figure 3.1) located on the beam rest, are designed to make any necessary adjustment.

Equality of swing. On release of the pan and beam rests, the pointer of an undamped balance will begin to oscillate. The distance of its swing to each side of the center of the pointer scale at the base should be approximately the same. Usually, some adjustment is necessary if there is a difference in distance of swing of more than two scale divisions. To make a change, the small nut on the beam (O in Figure 3.1) should be turned. Usually there is one of these nuts on each end, but some

[7] Craig, *Ind. Eng. Chem., Anal. Ed.* 11, 581 (1939); *Rev. Sci. Instruments* 16, 205 (1945); Kreider, *Ind. Eng. Chem., Anal. Ed.* 13, 117 (1941).

[8] Federal Specification for Balances; Analytical; AAA-B-92 (1949).

instruments have only one, located near the center. A small chain adjuster for this purpose is provided on some balances.

As mentioned later under the determination of the zero point, a damped balance is adjusted to make the pointer swing several scale divisions farther in one direction than the other.

Time of swing. All of the better instruments have some means of changing the center of gravity[9] of the swinging system. Although other means are used, the device most commonly employed is a small ring secured to the pointer by a set screw (*P* in Figure 3.1). The height may be regulated by loosening the set screw, moving the ring, and retightening the screw. The closer the ring is to the central knife-edge, the closer the center of gravity to the central knife-edge. Changing the center of gravity affects the time of swing required for a complete oscillation, that is, for the pointer to swing from one extreme to the other. The center of gravity must be dropped to decrease the time of swing. Balances adjusted for speed require 4 to 5 sec., and those for slow operation 10 to 12 sec.

Sensitivity. Changing the center of gravity also affects the sensitivity of a balance. The higher the center of gravity (up to the point at which the system becomes instable), the greater will be the sensitivity. Thus, moving the ring on the pointer upward usually increases the sensitivity of the balance, and moving it downward decreases the sensitivity. Since an increase in sensitivity increases the time of swing, the operator cannot adjust a balance for rapid weighing and at the same time take advantage of its maximum sensitivity. A good balance, set for rapid weighing, has a sensitivity of 2 to 3 (div./mg), whereas the sensitivity may be 5 or more when the time of swing is increased.

A sensitivity curve is necessary if weighings are made by a method that involves a calculation of the fourth (or fourth and fifth) decimal places from the known sensitivity. Such a curve can be constructed by determination of the deflection of the pointer produced by an excess load of 1 mg at each of several loadings of the balance pans. The zero point is determined for the empty balance (as described in Chapter 23); then a load of 1 mg is added to the right- or left-hand side by means of the rider or chain mechanism, and the zero point is determined a second time. The difference in zero points is the deflection resulting from an excess load of 1 mg at zero load on the balance. The sensitivity in terms of milligrams equivalent to one scale division is obtained by dividing 1 mg by the difference in scale divisions between the two

[9] See Moyer, *J. Chem. Educ.* 17, 540 (1940), for a method of determining the center of gravity.

zero points. In similar fashion, the zero points are determined with and without the addition of an excess load of 1 mg for loads of 10, 25, . . . 100 g on each of the balance pans. A chart is then constructed in which sensitivity is plotted against the load (see Figure 23.1, page 390).

An example will illustrate application of this practice in weighing. Suppose an object on the left-hand pan is not quite balanced with 20.12 g on the right-hand pan and the rider at 4.0 to the right. Moving the rider to 5.0 is too much. Obviously, the true mass lies between 20.1240 and 20.1250 g. The zero point is then determined with the rider at 4.0. Assume the value is 3.5 divisions to the right of the center of the scale, and that it was 0.0 originally, with no load on the pans. Also assume that the sensitivity is 5.0 with a 20-g load. Since, by definition, 1.0 mg would be required to cause a displacement of 5.0 divisions, an additional load of 3.5/5.0 mg would have to be added to bring the balance to the original zero point. The final weight is then

$$20.1240 + \left(\frac{3.5}{5.0} \times 1.0 \text{ mg}\right) = 20.1240 + 0.0007 = 20.1247 \text{ g.}$$

Relative arm length. In most balances the end knife-edge bearings are not exactly equidistant from the center knife-edge. This condition may be tested by weighing an object first on one pan and then on the other.

Small differences are of no significance in ordinary analytical work, reported on a percentage basis, as both the sample and any product thereof are weighed under similar conditions. If the balance is in error enough to affect the reliability of absolute values, correction may be made by use of the methods of double or substitution weighing, as described later.

Condition of knife-edges. The sharpness and general condition of the knife-edge bearings are important factors affecting the general operation of a good balance. In addition to inspection under a magnifying glass, one may test this condition by determining the sensitivity with the zero point first near the center of the scale, and then near the end. A dull knife-edge will be indicated by a lower value in the latter case, with the sensitivity expressed as div./mg.

Permanent adjustments. The adjustments mentioned above can all be made by an *intelligent* and *careful* worker. Certain other changes can be made, but they are sufficiently exacting that even the instructor should not attempt them unless he has the skill necessary for such repairs. These changes include such items as slight deformation of the beam, changes in the relative positions of the knife-edge bearings, and grind-

ing of the knife-edges. Such adjustments may be considered as more or less permanent.

WEIGHING

In connection with the operation of weighing, several items are important. The more significant of these are considered below.

Different methods of weighing are not to be confused with the procedures used in calculating or estimating the zero or rest point, treatment of which precedes the present discussion of the three procedures of weighing usually mentioned. (Operating directions are given in Chapter 23.)

Determination of the Zero Point

When the pan and beam rests are released, a properly adjusted undamped balance will usually start to swing, the pointer passing back and forth across the pointer scale. The distance traveled in successive swings is a little shorter each time, owing principally to the effects of bearing friction and damping of the air. Presumably the system would ultimately come to rest if undisturbed by external forces. The place on the scale at which the pointer would stop might be designated as the rest point.

In practical weighing on an undamped balance it would not be feasible to wait for the swinging pointer to come to rest, even if the balance environment were such that this state could be reached. Instead a point of reference on the pointer scale is determined. This point serves as a practical zero point.[10]

There has been considerable discussion regarding the order of release of the pan and beam rests preliminary to reading zero points. Some chemists favor releasing the pan rest first, whereas others favor prior release of the beam rest. Erratic swinging of the beam may result when the pan rests are released last, if they are not sufficiently well aligned. Accordingly, it is often preferable to release the pan rests first and then to lower the beam rest gently. As a result, the pointer will swing three to four divisions to either side of the zero point; this is a desirable working range.

Damped balances are handled somewhat differently. The swing-control adjustment is set to make the pointer swing several scale divisions farther in one direction than in the other. Then to determine the rest point the operator releases first the beam rest, then the pan rest. The pointer swings slowly in the direction of the longer deflection and stops

[10] Some writers use the words "swing" or "equilibrium" instead of "zero."

at the rest point. For this operation separate controls for the beam and pan rests are needed.

In Chapter 23, laboratory directions are given for the determination of such a zero point by three methods: single deflection, double deflection, and multiple swings. The first is the most rapid; the second is preferable for simple student balances; and the third is the most reliable for precise work.

Direct Weighing

The first, or ordinary, method consists in placing the object to be weighed on the left-hand pan, and weights to counterbalance it on the right-hand pan. This practice is always reliable when results on a percentage basis are sought, since any difference in length of the two arms of the beam is compensated.

Selecting the combination of weights to counterbalance the object is a fit-and-try operation. However, experience in weighing soon provides a basis for making reasonably close guesses.

When the absolute value of the mass of an object is sought, and the balance does not have an equal arm-length beam, a modified method must be used. Either the weighing can be made directly and the mass value multiplied by the ratio of the arm lengths or the method of double weighing or substitution weighing (as described later) may be used.

If the arm-length ratio is used, it should be determined immediately before or after weighing of the object the mass of which is sought. The ratio may vary with such conditions as unequal heat effects on the two arms.

Double Weighing

For very accurate work one method of weighing consists in weighing the object, first on one pan and then on the other. If $M =$ the true mass, $w =$ the weights required when the object is on the left-hand pan, $w' =$ the weights required when the object is on the right-hand pan, $r =$ the length of the right-hand arm, and $l =$ the length of the left-hand arm, the principle of moments indicates that

$$\begin{aligned} Ml &= wr \\ Mr &= w'l \\ M^2lr &= ww'lr \\ M^2 &= ww' \\ M &= \sqrt{ww'} \end{aligned}$$

The arithmetical mean of the two weights may be used when the difference between them is small. The method can be used only with

balances on which weighings can be made on either pan. The National Bureau of Standards uses a double keyboard balance for such routine weighings.

Double weighing may be used to determine the ratio of the arm lengths. If w = the weight used to counterbalance the object on the left-hand pan, Δw = the weight added to or subtracted from w when the object is weighed on the right-hand pan, r = the length of the right-hand arm, and l = the length of the left-hand arm, then

$$r/l = \sqrt{1 + \frac{\Delta w}{w}}$$

Substitution Weighing

For all ordinary balances the simplest procedure to avoid errors arising from unequal length of arms is weighing by Borda's method of substitution. In substitution weighing, the object is placed on either pan and counterbalanced with spare weights, lead shot, or other suitable material. Any convenient point is taken as the zero point. The object is then removed and weights are substituted until the same zero point is obtained. The weight value thus obtained is necessarily that of the object (disregarding buoyancy effects, discussed on page 40). This method should be used for the calibration of weights in Exercise 23.4 (page 389).

Sources of Error

In operating a balance and in handling objects being weighed, the operator should keep in mind several common sources of error. Basic requirements for accurate weighing are that the balance be in proper adjustment, that the object to be weighed be chemically stable, and that the object be handled without contamination by fingerprints, which may leave a determinable mass of dirt and grease.

The object should be at balance (room) temperature when weighed. If it is too hot (cold), an upward (downward) current of air will result, causing a negative (positive) error in weighing data. Thus, Blade[11] reports an error of 0.19 mg for each degree of temperature difference between a porcelain crucible and the balance pan.

Electrification of certain bodies during handling, e.g., in wiping glass vessels, may cause error. Such objects must be allowed to stand in the balance case long enough for the charge to be dissipated. Some analysts recommend the use of a slightly dampened cloth for wiping

[11] *Ind. Eng. Chem., Anal. Ed.* **12**, 330 (1940).

glassware. Time (20 to 30 min.) must then be allowed for atmospheric equilibrium to be reached before weighing.

The moisture film to be found on most objects varies. An object kept in a desiccator may vary in weight a few tenths of a milligram on different days. In precise work, or in work involving the use of large objects such as glass absorption vessels, this problem may necessitate use of a tare object of the same material, having about the same surface area, and treated in the same way as the object whose weight is sought. The tare object is placed on the right-hand pan, along with any additional weights needed.

Since weighing is done in air, the weighing results for all objects, except those having the same density as the weights used, will carry buoyancy error. Objects less dense than the weights displace more air than the latter, and, consequently, weighing results for these objects will contain a negative error. The opposite effect occurs with objects more dense than the weights. In precise weighing, this error must be considered. The magnitude of the correction is obtained by calculation of the difference in the weights of air displaced by the object and the weights; its sign (+ or −) depends upon the relative densities of the two. Application of this method of correction will be illustrated in Chapter 4 where directions are given for calculating the amount of water to use for calibration purposes. The general method of calculation of buoyancy correction is presented in Chapter 33, in connection with the problems on the determination of mass values. A convenient nomographic chart for making such corrections is described by Thacker.[12]

ANALYTICAL WEIGHTS

Most sets of analytical weights have, as their largest piece, one of 100-g or 50-g denomination; the smallest is the 1-mg piece, although, as a rule, even the 5-mg piece is not used unless the beam has less than 10 major divisions. The best distribution of pieces in a set came into use only recently. Starting with the 50-g piece, the order runs as follows: 50, 30, 20, 10; 5, 3, 2, 1 g; and 500, 300, 200, 100; 50, 30, 20, 10; 5, 3, 2, 1 mg. In this distribution there are five groups of four each, the corresponding member of each succeeding group having one-tenth the value of that of the preceding group. In many older sets the fractional pieces are marked in fractions of a gram instead of in milligrams, so that the 500-mg piece, for example, is marked 0.5 g.

Many sets in use have a 5, 2, 1, 1 distribution, which means that at least four pairs of pieces have the same denomination. In most cases

[12] *Ind. Eng. Chem., Anal. Ed.* 16, 275 (1944).

the individuals of a pair do not have the same value. This arrangement necessitates marking and distinction in use if the calibration values are to be used in careful work.

One should take care not to injure the plating or lacquer of weights.

Classes

The National Bureau of Standards approves two classes of weights. They differ in construction and in tolerances (permissible error).

In Class M sets, intended for use in the accurate determination of absolute mass, the gram pieces are made of a single piece of metal. In Class S sets, used in all ordinary precise weighing, such pieces consist of a large part or base, into which the handle or top is screwed.

TABLE 3.1

PRECISION OF CORRECTIONS AND TOLERANCES
(in milligrams)

	CLASS M		CLASS S	
Denomination	*Precision of Corrections*	*Tolerance*	*Precision of Corrections*	*Tolerance*
100 g	0.1	0.5	*0.5 or 0.1	0.5
50	0.1	0.3	0.1	0.3
20	0.01	0.2	0.1	0.2
10	0.01	0.15	0.05	0.15
5	0.01	0.15	0.05	0.15
2	0.01	0.10	0.05	0.10
1	0.01	0.10	*0.05 or 0.01	0.10
500 mg	0.001	0.05	0.01	0.05
200	0.001	0.05	0.01	0.05
100	0.001	0.05	0.01	0.05
50	0.001	0.03	0.01	0.03
20	0.001	0.03	0.01	0.03
10	0.001	0.02	0.01	0.02
5	0.001	0.02	0.01	0.02
2	0.001	0.01	0.01	0.01
1	0.001	0.01	0.01	0.01

* Single reference standards of these denominations will be certified to the higher degree of precision indicated.

All of these tolerances are slightly smaller in the latest report. See "Precision Laboratory Standards of Mass and Laboratory Weights," NBS Circular 547 (1954).

Brass and Tobin bronze have been widely used as the base metal for all gram pieces. They are then plated with platinum, gold, or chromium, or are covered with a hard lacquer. Nonmagnetic, stainless alloys are coming into increasing use as materials for gram pieces.

The fractional pieces are solid metal. In the best sets all pieces are platinum. Gold and tantalum are also used for pieces down to the 30- or 20-mg size. In most sets aluminum is used for pieces from 30 to 1 mg.

Riders are made of either platinum or aluminum. Balances will be encountered that require 12-, 10-, 6-, or 5-mg riders. It should be kept in mind that the rider required for a given balance should weigh (in milligrams) an amount equal to the major division on the beam situated *over* the end knife-edge if the zero mark is in the center of the beam, or one-half of this value if the zero mark is over the left-hand knife-edge and the 10 mark, for example, is over the right-hand knife-edge.

In addition to specifying materials and design of weights, the National Bureau of Standards has established certain limits for error in Class M and Class S sets. The data in Table 3.1 show these tolerances.

Calibration

Unless a set of expensive weights that meets the specifications of Class S or M pieces is secured, the values for the weights are likely to be sufficiently in error to necessitate calibration before the set is used for any careful weighing.

Calibration or testing of weights may be done in several ways. In laboratories having no standard, a relative method may be used. This method is entirely satisfactory unless absolute values are required in determining the mass of an object to be weighed. In relative calibration, one weight, e.g., the 1-g piece, is assumed to have a given value, such as 1.0000 g. The value of each of the other pieces is then determined in terms of the assumed standard, and a series of corrections is calculated for use in making weighings.

If the weights are to be accurate for all situations, they should be calibrated on an absolute basis, that is, in terms of the standard of mass, the kilogram. In this method an object of known mass is required. In the commonly recommended procedure of absolute calibration, known as Richards' method,[13] a single standard piece is used in much the same way that one piece is used in the relative method mentioned above. This is a laborious procedure, requiring considerable calculation to check all the interrelations of the pieces, but it is reliable if done by a skilled operator. Various modifications have been proposed for Richards' original procedure.[14]

[13] *J. Am. Chem. Soc.* **22**, 144 (1900).

[14] See Blade, *Ind. Eng. Chem., Anal. Ed.* **11**, 499 (1939); Hurley, *Ind. Eng. Chem., Anal. Ed.* **9**, 239 (1937); MacNevin, *J. Chem. Educ.* **22**, 406 (1945); Thornton, *J. Chem. Educ.* **14**, 270 (1937).

The author's preferred method of calibration involves checking each piece of a set against a corresponding piece from a set calibrated by the National Bureau of Standards. In this method no calculation is involved to determine the value of a piece in terms of one of a different denomination, with the attendant possibility of multiplying small errors.

Regardless of the method used, comparisons should be made using the substitution method of weighing. The balance employed should be the best available. If possible, the fractional pieces should be checked on an assay (or micro) balance on account of its greater sensitivity. Corrections should be calculated for each piece and these values listed, marking them negative if the weight's mass as calibrated is less than its marked value, and positive if the reverse is true. These values may be placed on a card in the rear of the balance case for convenient reference. Their use for accurate work necessitates a summation of the several corrections and an application of the result for each weighing.

Adjustment

When many weighings are made, the total time required to apply corrections becomes appreciable. Inconvenience and loss of time may be avoided by use of sets adjusted to the tolerance specified for Class S weights. This procedure requires little more time than a single calibration, if a weight-adjusting set is used. A set adjusted in this way in the author's laboratory was found by the National Bureau of Standards to have 0.05 mg as the largest correction. The adjusted weights should be checked occasionally. Figure 3.6 illustrates such adjusting equipment.

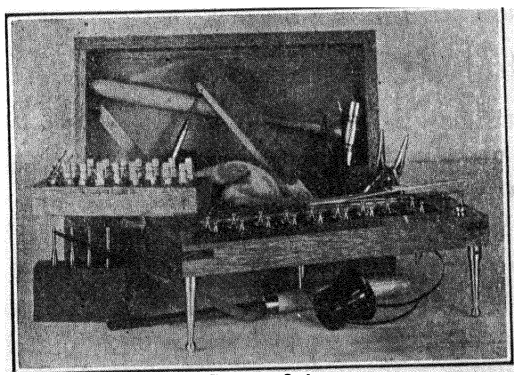


Figure 3.6

Thompson weight-adjusting apparatus (courtesy Thompson Balance Co.).

CHAPTER 4

MEASUREMENT BY VOLUME

Although liquid samples are sometimes weighed, the measurement is more often by volume. Measurement by volume is even more generally used for gaseous samples. However, since the methods of general gas analysis are not included in this book, discussion will be limited for the most part to problems in volumetric measurement of liquids.

The discussion that follows is intended to be sufficiently complete to cover the use of volumetric ware in initial measurement of liquid samples and in subsequent measurement of systems in the liquid state encountered in determining constituents by different methods. *This use includes all titrimetric measurements on a volume basis.*

MATERIALS OF CONSTRUCTION OF VOLUMETRIC WARE

Formerly, soft lime glass was used exclusively for the fabrication of glass volumetric ware, much of which was imported from Europe. The use of borosilicate glass by American manufacturers of volumetric ware is becoming increasingly popular. Wichers, Finn, and Clabaugh[1] have made a thorough study of the various brands of the latter type of glass from the viewpoint of its applicability in chemical glassware.

Soda-lime glasses are easily shaped over a burner, and may be heated and cooled many times without discoloration. Etching of this glass with hydrofluoric acid produces fine, deep lines with a rough surface. Fine lines promote accuracy in reading graduations, and opaque colored fillers, which adhere readily to the rough surface, facilitate reading. Such glass is first choice for burets, on which sharp lines are desirable; resistance to heat shock is unimportant, and attack on the glass by common titrants is negligible. It is also, in most cases and for the same reasons, the best glass for pipets, volumetric flasks, and similar ware.

[1] *Ind. Eng. Chem., Anal. Ed.* 13, 419 (1941).

Pyrex brand glass and Kimble N-51A glass are representative of borosilicate glasses. They are preferred for volumetric ware in which resistance to heat shock is required, and for ware to contain liquids that change readily through interaction with traces of substances dissolved from the glass, particularly at elevated temperatures or after long storage. Thus, condensers that must withstand heat shock, and containers for neutralization indicators should be of borosilicate glass to prevent chemical change during use.

TYPES AND USES OF VOLUMETRIC APPARATUS

The three pieces of apparatus used most by the analyst for measuring liquids are known as *volumetric flasks, pipets,* and *burets.* Common forms of each of these pieces are described. Throughout this chapter emphasis is placed on recommendations made by the National Bureau of Standards[2] for such ware.

Flasks

The volumetric flask is, in its general form, a pear-shaped, flat-bottomed bulb with a slim neck. The N.B.S. preferred form is illustrated in Figure 4.1A. The Giles form is illustrated in Figure 4.1B. In the latter, the supplementary bulb in the neck has a capacity one-tenth that of the main bulb. The capacities of volumetric flasks usually range from 10 to 2000 ml.

Such flasks are used in a variety of ways, primarily for preparing standard titrimetric solutions or for diluting samples to a given volume from which a simple fraction, known as an aliquot, may be taken.

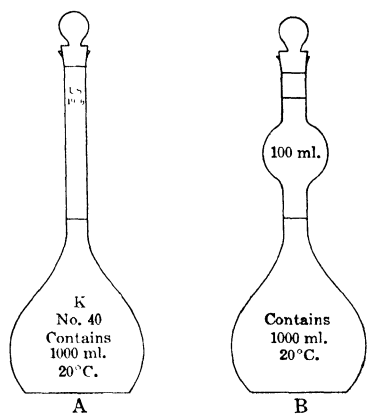


Figure 4.1

Types of volumetric flasks.

Pipets

The types of pipets most commonly used are diagrammed in Figure 4.2. Figure 4.2A is a diagram of the common form of transfer pipet, Figure 4.2B is the Ostwald-Folin form used in biochemistry, and Figure 4.2C is the Mohr measuring form. Pipets usually range in capacities from 1 to 200 ml, although the measuring type seldom exceeds 50 ml.

[2] To save space, the abbreviation N.B.S. will be used frequently for National Bureau of Standards.

The general use of these types of pipets is indicated by their names. The transfer type serves for transferring a single volume, such as 1, 5, or 10 ml, of liquid from one vessel to another. Occasionally ware of this type, such as the Mahin milk pipet,[3] is made to deliver some special volume of liquid, e.g., 17.6 ml. In general, transfer pipets are used to measure liquids or solutions the volumes of which must be known precisely as, for example, addition of a known amount of standard solution.

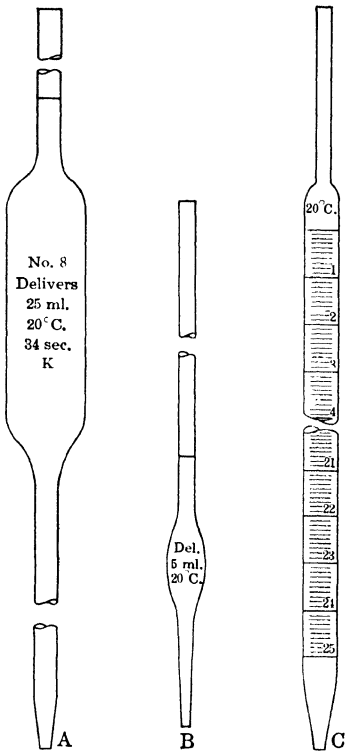


Figure 4.2
Types of volumetric pipets.

The measuring type of pipet serves for transferring liquids where the volume desired involves fractional parts of milliliters, or amounts not conveniently obtainable with transfer pipets. In general, they serve for adding volumes of reagents where greater precision of measurement than that given by a measuring cylinder is necessary, but where the volume is not to be used in the calculations for the desired result.

Burets

Volumes and, less frequently, masses of liquids are measured by means of burets, general types of which are illustrated in Figure 4.3. Their primary use is in titrimetric procedures to measure the amount of standard solution required in a titration. As Figure 4.3 shows, burets made for measuring volume are considerably different in design from those measuring mass of liquids.[4]

Many different variations in design and arrangement have been made to secure rapid and efficient transfer of the standard solution into and out of burets for routine work. One type of commercial ware is illustrated in Figure 4.4. By means of a rubber bulb, air is forced into the reservoir of solution in order to elevate the liquid into the top of the

[3] *Ind. Eng. Chem.* **15**, 943 (1923).
[4] Weight burets have no essential connection, of course, with volumetric ware. For their merits, see Washburn, *J. Am. Chem. Soc.* **30**, 39 (1908).

buret. When the buret is filled and the air pressure released, the excess solution siphons back to the reservoir, leaving the top of the liquid column in the buret at zero.

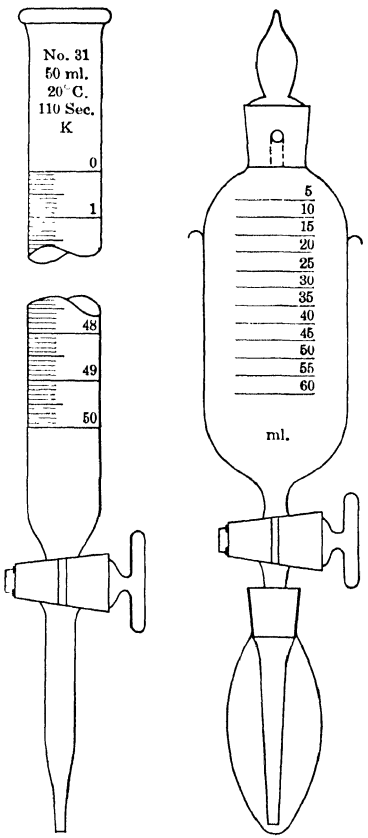
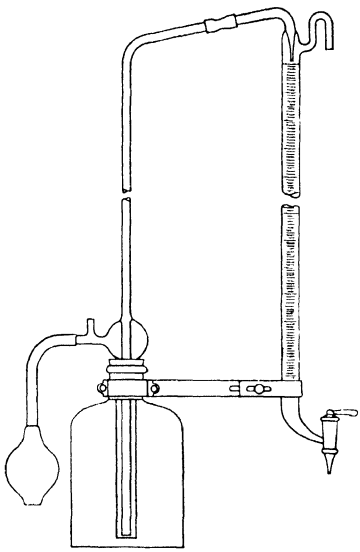


Figure 4.3 (left)

Types of volume and weight burets.

Figure 4.4 (below)

Buret with reservoir.



SPECIFICATIONS FOR VOLUMETRIC WARE

In order to provide a sound basis for efficient and reliable titrimetric measurements, the National Bureau of Standards has drawn up[5] a series of specifications for volumetric ware. Class A ware, as defined in the Federal Standard Stock Catalog,[6] conforms to these specifications. Class B ware is also described in the catalog. Figures 4.1, 4.2, and 4.3 illustrate the important design features of volumetric apparatus, and the

[5] *Nat. Bur. Standards Circ.* 434 (1941), "Testing of Glass Volumetric Apparatus."
[6] Federal Specification for Volumetric Apparatus; Glass; DD-V-581 (1937).

inscription of the different kinds of ware according to N.B.S. recommendations.

Excerpts from N.B.S. Circular 434 are given below. It may be pointed out that certain of the specifications in the circular represent a compromise between different possibilities, in order that a practical set of standards requiring a minimum of time and expense may be established.

General, workmanship, and marking. The liter and the one-thousandth of the liter, called the milliliter, are employed as units of capacity. In all volumetric work, the unit of volume employed is the milliliter and not the cubic centimeter.

Twenty degrees centigrade is regarded by the Bureau as the standard temperature for glass volumetric apparatus.

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

Stoppers and stopcocks must be so ground as to work easily and to prevent leakage. The parts on which graduations are placed must be cylindrical for at least 1 cm on each side of every mark, but elsewhere may be enlarged to secure the desired capacities in convenient lengths.

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

The clear space between two adjacent marks must not be less than 1 mm. The spacing of marks on completely subdivided apparatus must show no evident irregularities, and sufficient divisions must be numbered to indicate readily the intended capacity of any interval.

TABLE 4.1

DIAMETERS OF FLASK NECKS

Capacity of Flask up to and including (in ml)	*Maximum Diameter* (in mm)	*Minimum Diameter* (in mm)
25	8	6
50	10	6
100	12	8
200	14	9
250	15	10
500	18	12
1,000	20	14
2,000	25	18
4,000	35	22
6,000	45	30

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

Every instrument should bear the name or trade-mark of the maker. Every instrument must bear a permanent identification number, and detachable parts, such as stoppers, stopcocks and the like, belonging thereto, must bear the same number.

Shapes and dimensions. At the capacity mark or marks on a flask the inside diameter should be within the limits [given in Table 4.1].[7]

The neck of a flask must not be contracted above the graduation mark.

The capacity mark on any flask must not be nearer the end of the cylindrical portion of the neck than specified [in Table 4.2].

TABLE 4.2

FLASK GRADUATIONS

Capacity	*Distance from Upper End* (in cm)	*Distance from Lower End* (in cm)
100 ml or less	3	1
More than 100 ml	6	2

A flask may be graduated both to contain and to deliver, provided the intention of the different marks is clearly indicated, and provided the distance between the two marks is not less than 1 mm.

The suction tube of each transfer pipet must be at least 16 cm long, and the delivery tube must not be less than 3 cm nor more than 25 cm long.

The inside diameter of any transfer pipet at the capacity mark must not be less than 2 mm and must not exceed the limits [given in Table 4.3].

TABLE 4.3

DIAMETERS OF PIPET STEMS

Capacity, up to and including (in ml)	*Diameter* (in mm)
25	4
50	5
200	6

[7] Specifications for the Giles type of flask are not included here, although they are given in Circular 434.—*Author.*

The outside diameter of the suction and delivery tubes of transfer pipets, exclusive of the tip, must not be less than 5 mm.

The capacity mark on transfer pipets must not be more than 6 cm from the bulb.

Only burets and measuring pipets emptying through a nozzle permanently attached at the bottom are accepted for test.

So-called Schellbach burets, that is, those having a milk-glass background with a colored center line, will not be accepted for test on account of possible errors due to parallax.

The distance between extreme graduations must not exceed 70 cm on burets nor 35 cm on measuring pipets.

The upper end of any measuring pipet must not be less than 10 cm from the uppermost mark and the lower end not less than 4 cm from the lowest mark. On 50-ml and 100-ml burets the highest graduation mark should not be less than 4 cm nor more than 10 cm from the upper end of the buret. On burets having a capacity of 25 ml or less this distance should not be less than 3 cm nor more than 6 cm.

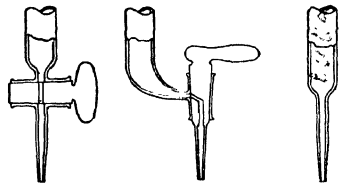


Figure 4.5

Types of buret and pipet tips.

Buret and pipet tips should be made with a gradual taper of from 2 to 3 cm, the taper at the extreme end being slight. A sudden contraction at the orifice is not permitted and the end of the tip must be ground true, with a smooth, plane surface, and finished with a polish or semipolish. In order to facilitate the removal of drops and to avoid splashing when the instrument is vertical, the tip may be bent slightly. Approved forms of tips for burets, measuring pipets, and transfer pipets are shown in Figure 4.5.[8]

Rates of delivery. The outlet of any transfer pipet must be of such size that

TABLE 4.4

MINIMUM OUTFLOW TIME FOR PIPETS

Capacity, up to and including (in ml)	*Outflow Time* (in sec.)
5	15
10	20
50	30
100	40
200	50

[8] It is good experience for the student to attempt to draw the tip for the wash bottle to conform to those shown in Figure 4.5.—*Author.*

the free outflow shall last not more than 1 minute and not less than the time for the respective sizes [given in Table 4.4].

The rate of outflow of burets and measuring pipets must be restricted by the size of the tip and for any graduated interval the time of free outflow must not be more than 3 minutes nor less than those given in Table 4.5 for the respective lengths.

TABLE 4.5

MINIMUM OUTFLOW TIME FOR BURETS

Length Graduated (in cm)	*Outflow Time* (in sec.)	*Length Graduated* (in cm)	*Outflow Time* (in sec.)
70	160	40	70
65	140	35	60
60	120	30	50
55	105	25	40
50	90	20	35
45	80	15	30

Tolerances. The error of the indicated capacity of any 10 consecutive subdivisions must not exceed one-fourth the capacity of the smallest subdivision. Tolerance may be defined as the maximum permissible error. Table 4.6 indicates the values established by the National Bureau of Standards for flasks, pipets, and burets.

TABLE 4.6

TOLERANCES
(in milliliters)

	LIMIT OF ERROR			
		Pipets		
Capacity, less than and including	*Flasks*	Transfer	Measuring	*Burets*
2		0.006	0.01	
5		0.01	0.02	0.01
10		0.02	0.03	0.02
25	0.03	0.03	0.05	0.03
50	0.05	0.05	0.08	0.05
100	0.08	0.08	0.15	0.10
200	0.10	0.10		
500	0.15			
1000	0.30			
2000	0.50			
4000	1.00			
6000	1.50			

MANIPULATION OF VOLUMETRIC WARE[9]

Certain essential points in the manipulation of volumetric apparatus must be observed in order that reliable measurements may be obtained.

Cleaning and Cleanliness

The most important requirement in the use of volumetric ware is cleanliness. Uniform wetting of the glass surface of a vessel is a test of its cleanliness. This point is especially important in burets and pipets, which should always be watched for nonuniformity in drainage, evidenced by drops of liquid adhering to the inside surface. Directions for preparing and using cleaning media are given in Chapter 24.

Alkaline solutions stored in glass for more than short periods of time attack the glass by dissolution action. Etching occurs, and often a colloidal precipitate of hydrated silica or sodium silicate is formed. Measuring glassware should be rinsed and cleaned immediately after it has been used for alkaline solutions. This is particularly important in the case of burets in order to prevent action on the ground glass surface of the stopcock. The action on glass of alkaline standard solutions is one reason for their changing concentration with time.

Reading the Meniscus

In all apparatus where the volume is limited by a concave meniscus, as with aqueous solutions, the reading or setting is made on the lowest point of the meniscus. In order that the lowest point may be observed most easily, some dark surface should be placed immediately below and back of the curved surface of the solution. This makes the profile of the meniscus dark and thus clearly visible against a light background. Various devices have been suggested as aids.[10] Possible error of parallax may be avoided by having the ware graduated and used in conformity with specifications on this point.

Regulating the Outflow

The time of outflow of burets and pipets should be reasonably close to the N.B.S. specification. If outflow is too fast, the tips should be redrawn, care being taken to make them conform as closely as possible to the approved form. Redrawing pipet tips necessitates recalibration. If outflow is too slow, titrations are unduly prolonged. To speed outflow, the tips may be enlarged by grinding back a short distance. The piece is held so as to bring its axis vertical with the tip resting on a car-

[9] See the pamphlet, "The Care and Handling of Glass Volumetric Apparatus," by the staff of the Kimble Glass Co.

[10] Several types of meniscus readers are described in Chapter 24.

borundum stone; an easy, rotary motion of the tip results in the desired grinding.

Burets with well-made stopcocks, properly lubricated, may be tested for leakage by setting the meniscus at zero. No appreciable change in the level of the meniscus should be evident within 5 minutes. Lubricants and lubrication are discussed in Chapter 24.

Handling Liquids

Burets are used for delivery of liquids; pipets are usually used for the same purpose and flasks are used to contain liquids. Since, occasionally, pipets are used to contain and flasks to deliver, such pieces may have marks for both purposes.

The following suggestions are excerpts from the previously cited N.B.S. Circular 434:

In filling flasks the entire interior of the vessel will be wetted. A drainage time of about 2 minutes should be allowed before completing the adjustment of the meniscus to the mark.

In filling pipets and burets excess liquids adhering to the tip should be removed when completing the filling.

In emptying burets they should be held in a vertical position, and after the continuous unrestricted outflow ceases, the tip should be touched with the wet surface of the receiving vessel to complete the emptying. Transfer pipets should be held in a vertical position and the outflow should be unrestricted until the surface of the water reaches the upper end of the delivery tube; the tip should then be touched to the wet surface of the receiving vessel and kept in contact with it until the emptying is complete.

The water remaining in the tip should not be blown out.

Stopcocks should be completely open during delivery.

Burets and pipets should be filled to about 2 cm above the zero, and the setting to the zero mark made by slowly emptying from this point.

While under normal usage the measurements ordinarily are from the zero mark, other initial points may be used on burets of standard form.

Provision for Temperature Variations

In Chapter 12 mention is made of the important effect temperature changes have upon the volume of liquids, and suggestions are made for applying necessary corrections. Although volumetric ware may be calibrated for any given workable temperature, the N.B.S. standard temperature is 20°C. The student should not forget that N.B.S. calibrations are correct only at this temperature. The error at any other temperature will result from the difference in coefficients of expansion of glass and of the solution or liquid in the vessel.

TESTING AND CALIBRATION

Flasks, pipets, and burets with N.B.S. certificates may be purchased, but many laboratories cannot afford such equipment. Although the best grade of ware from reputable supply houses is reasonably reliable, the analyst should maintain a skeptical attitude toward all pieces the values of which he does not know. In particular, he never knows when the tip of a pipet may have been redrawn, thus ruining the reliability of the ware. Such pieces should be checked before use by careful measurement.[11] The student should consider calibration of instruments of measurement as part of his training, and as a safeguard against this kind of error.

Calibration, in its general sense, refers simply to a determination of the value of the device calibrated, whether the item be a pipet, an ammeter, or a surveyor's tape. In volumetric work calibration sometimes implies both measurement and adjustment to a given value. Thus, calibration may reveal that a vessel is incorrectly marked and, as a result, a new mark must be located.

To check volumetric ware, one has a choice of (1) determining the mass of liquid contained or delivered by a given piece, or (2) comparing the piece with a piece previously calibrated. As each method has certain advantages, both are described.

Preferably, volumetric ware is calibrated with the liquid to be measured in it, but this procedure is not always feasible. Since most titrants are dilute aqueous solutions, with surface tensions and viscosities near those for water, water is usually specified as the test liquid. It should be distilled, of course, and then boiled before using, to remove absorbed gases.

Metric Standards of Measurement

The definitions of the standards of measurement employed in the metric system should be kept clearly in mind. The two fundamental standards are length and mass, and the two derived standards are area and volume.

The standard of *length* is the meter,[12] defined as the distance between the two defining lines on the international platinum-iridium bar at the temperature of melting ice. Subdivisions of the meter, particularly the centimeter and the millimeter, are widely used in chemical specifications.

[11] Moran, "Testing Volumetric Glassware," *Proc. Am. Soc. Testing Materials.* **41**, 492-497 (1941).

[12] According to Briggs, *Rev. Modern Phys.* 11, 111 (1939), the U.S. standard meter bar, furnished in 1875, has changed only 0.001 mm in length, or one part in 10^9 parts, in comparison with the international standard.

The distance between the defining lines on the meter bar has been known for some years in terms of the wave length of one of the cadmium spectrum lines, 6438.4696 *A*. A late recommendation of this kind is the use of the line at 5460.7532 *A* for the isotope of mercury of mass 198 prepared by transmutation from gold.[13]

The standard of *area* is the square meter. Only the areametric method of quantitative analysis employs this standard, and such a method is little used.

The standard of *mass* is the kilogram,[14] the international piece being a platinum-iridium alloy. Although the kilogram was originally intended to equal the mass of a cubic decimeter of pure water (at the temperature of maximum density), and so be related to the standard meter, later measurement revealed that the masses were in fact not equal.

Because of the mistake made in establishing the mass of the kilogram piece, we now have *two* standards of *volume*. The first standard is a cube the edge of which is 1 meter in length, the *cubic meter*. The millionth-part subdivision of the cubic meter is the cubic centimeter. Thus, the familiar "cc" is related to the standard meter, and *not* to the liter.

The second standard is the *liter,* defined as the volume occupied by the mass of 1 kilogram of pure water at the temperature of its maximum density and under a pressure of 1 atm. The thousandth-part of a liter, therefore, is a milliliter, *not* a cubic centimeter. Since 1 liter equals 1000.028 cc, the difference is significant only in the most refined work. Sometimes the liter is referred to as a unit of capacity.

It may be mentioned that the isotopic composition of the "pure water," used in the original work on the standards, and hence the exact density, must remain an uncertainty. We can assume only that the water consisted of the naturally occurring isotopic mixtures of hydrogen and oxygen. To clear the difficulty today the alternatives seem to be (1) to abandon the liter and use the cubic decimeter instead, or (2) to prepare carefully a sample of one of the waters of definite isotopic composition, such as $H^1{}_2O^{16}$, and to repeat the measurements.

Calibration by Weighing

In calibration by weight the amount of water contained in, or delivered by, a given piece of apparatus is weighed. To calibrate a liter flask under the conditions for which the liter is defined would require 1000 g of water. These conditions are so difficult to attain experimentally that

[13] Meggers, *J. Opt. Soc. Amer.* **38**, 7 (1948); **40**, 737 (1950).

[14] Briggs, *loc. cit.* The U.S. standard of mass, kilogram No. 20 furnished in 1875, has changed by only one part in 50,000,000 in nearly 60 years.

it is much simpler to work under the conditions prevailing in the ordinary laboratory, and then to calculate corrections for density, buoyancy, and expansion of glass (see Chapter 24).

To illustrate this method of calibration, assume that the problem is to calculate the mass of water to weigh into a liter flask at 30° so that the mark will be correct at 20°, using brass weights and taking 0.000025 as the coefficient of cubical expansion for the glass vessel. The first correction is for density, as the working temperature is 30°. At this temperature the density of water (see Table 4.7) is 0.99568. If this were the only correction, 995.68 g of water should be taken.

The second correction is for the buoyant effect of the air upon the water and the weights. The water weighs less in air than in a vacuum. The resultant correction is the difference between the two buoyant effects,

TABLE 4.7

WEIGHT OF 1 LITER OF WATER AT DIFFERENT TEMPERATURES
(corrected for buoyancy and glass expansion)

Temperature (in °C.)	*Weight, Corrected for—*		
	Density Only	*Density and Buoyancy*	*Density, Buoyancy, and Glass Expansion*
4	1000.00*		
15	999.13	998.05	997.93
16	998.97	997.90	997.80
17	998.80	997.74	997.66
18	998.62	997.56	997.51
19	998.43	997.38	997.36
20	**998.23**	**997.18**	**997.18**
21	998.02	996.97	996.99
22	997.80	996.76	996.81
23	997.56	996.52	996.60
24	997.32	996.28	996.38
25	997.07	996.04	996.16
26	996.81	995.76	995.91
27	996.54	995.49	995.66
28	996.26	995.21	995.41
29	995.97	994.92	995.14
30	995.67	994.62	994.87
31	995.37	994.32	994.60
32	995.05	994.00	994.30
33	994.73	993.68	994.00
34	994.40	993.35	993.70
35	994.06	993.01	993.38

* Move the decimal point three places to the left to obtain the density of water at the respective temperatures.

each of which is equal to the weight of the air displaced by the object and by the weights. Obviously the liter of water displaces a liter of air. This volume weighs different amounts, depending upon several factors among which are temperature, pressure, and relative humidity.[15] For the present purpose an average value of 1.19 g (for 750 mm and 20°) may be taken. The volume of air displaced by the weights is obtained by dividing the mass (995.68 g) by the density of brass (8.4); this gives 118.5 ml with a weight of 0.14 g. Subtracting this amount from 1.19 g leaves 1.05 g as the buoyancy correction. This amount subtracted from 995.68 g leaves 994.63 g, the correct amount if the flask were calibrated at 30° and were to be used at 30°.

The third correction takes into account the expansion or contraction of the glass vessel as the working temperature is above or below 20°. At 30° the increase in volume of the flask is $1000 \times 10 \times 0.000025 =$ 0.25 ml. Multiplying this volume by the density of the water at 30° gives 0.25 g. Adding this amount to 994.63 gives 994.88 g as the weight of water to be used to locate a mark at 30° that will be correct at 20°.

Table 4.7 gives the weights of water to be used at different temperatures for a liter of water. *These are all calculated for an average value of 1.19 g as the weight of a liter of air.*[16]

Calibration by Comparison

Where facilities are available, volumetric ware may be calibrated conveniently by comparison with previously standardized pieces. This method is especially desirable where calibration is a routine practice for many pieces.

For this work Morse and Blalock[17] proposed bulbs of a design which later received N.B.S. approval. Laboratories equipped with such devices keep them assembled for student use. The N.B.S. arrangement, together with the method recommended for calibrating the bulbs, is shown in Circular 434. Different sizes of bulbs, illustrated in Figure 4.6, provide for burets and flasks of all capacities. For burets several designs of calibrating pipets have been proposed.

In checking apparatus by means of these devices boiled water is obviously unnecessary and temperature is not a significant factor so long as it does not change appreciably during the comparison. Directions are

[15] See Chapter 33 for problems on the determination of mass values, where account is taken of the effects of temperature and pressure on the mass of unit volume of air.

[16] See *British Standards* 1797, of the British Standards Institute, for tables showing conversion of weights of water or mercury to volume, for a range of temperatures and for both soda and borosilicate glass vessels.

[17] *Am. Chem. J.* 16, 479 (1894).

given in Chapter 24 for using this method. It is assumed that the instructor will have the apparatus assembled for use.

Thompson has described apparatus for calibrating volumetric ware by

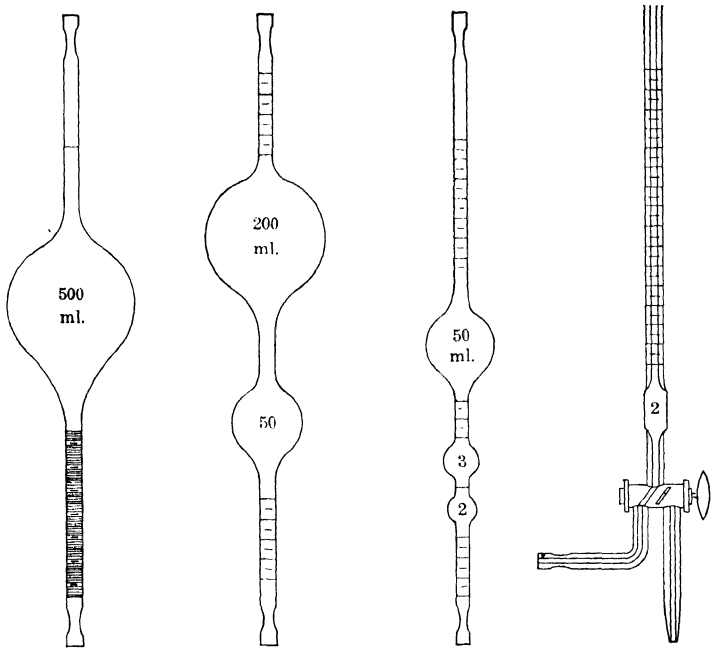


Figure 4.6

Calibrating pipets.

the comparison method.[18] The measurement is made in the standard pipet with a liquid which does not wet glass (mercury), thus avoiding error resulting from drainage.

[18] *Ind. Eng. Chem., Anal. Ed.* **14**, 268 (1942).

CHAPTER 5

PRELIMINARY TREATMENT

As already stated, most samples must be measured as the first step in a quantitative analysis. The analyst often proceeds next with the sample as such to any necessary separation(s) and/or to the final measurement of the desired constituent(s). Procedures which include no pre-separative or pre-measurement treatment, for example, are the determination of moisture in coal and of the specific gravity of milk. Much more frequently, however, the sample must be subjected to some kind of preliminary treatment before it is suitable for subsequent operations. This chapter is a brief introduction to treatments used more or less frequently in analyses. Some of the illustrative examples given here, as well as others, are discussed more fully in Chapters 25 to 31. Analogous cases are widely scattered throughout the literature of applied analytical methods.

CONCENTRATION

Some samples, such as water of low mineral content, contain so little of the desired constituents that the analyst concentrates them to smaller volumes in order to obtain more concentrated solutions with which to work. In water analysis this operation of evaporation is performed, preferably, in platinum or fused silica vessels to prevent contamination by action of the water on the vessel.

DISSOLUTION

Occasionally a method of separation can be applied directly to a solid, as in the determination of the "loss on ignition" of limestone (Exercise 31.2). Likewise, some measurements, such as density and electrical conductivity, can be made directly on samples such as binary alloys. More striking, of course, is the example of sparking or arcing a polycomponent

alloy, such as Dow metal, in methods employing emission spectrometry (see Chapter 19). The great majority of solid samples, however, must be brought into solution, because under these conditions the operations and transformations necessary in many analyses are best accomplished.

Selection of the solvent depends principally upon the nature of the sample and upon the disposition to be made of the solution. Water is undoubtedly first choice as a solvent, as it is the most generally useful compound for this purpose. Conventional schemes of inorganic qualitative and quantitative analysis are based largely upon the handling of systems in aqueous solution. However, there are many natural and artificial products (e.g., rocks, ores, plastics, and ceramic and metallic products) that do not dissolve in water to any useful extent. Because the solubility of so many substances in pure water is very low, a more reactive solvent, such as an aqueous solution of an acid or a base, must often be used. After water, the dilute acids, such as hydrochloric, nitric, sulfuric, and perchloric, are probably the most useful solvents. Perchloric acid is used less commonly than the others, but its desirable properties have brought it into wide use in certain operations.[1]

Various factors are important in deciding which acid should be used. A few examples will illustrate this point. In brass analysis (Exercise 31.3) nitric acid dissolves all of the usual constituents except tin, which is converted to hydrous stannic oxide, $SnO_2 \cdot xH_2O$, in the course of dissolution of the other constituents. The insoluble oxide may then be filtered off and dehydrated for weighing. Hydrochloric acid is a good solvent for evolving carbon dioxide from limestones. However, in this procedure the loss of acidic vapors on boiling the solution (Exercise 28.2) must be allowed for. Possible vaporization of hydrogen chloride, along with the carbon dioxide, necessitates inclusion of an absorbent in the train for this unwanted gas. The use of either sulfuric or perchloric acid prevents this difficulty. However, sulfuric acid does produce insoluble calcium sulfate, if the calcium content of the limestone is high. This insoluble matter may then prevent complete attack of the acid on the limestone.

Concentrated acids may be the best in some situations. For example,

[1] Caution should be exercised in the use of perchloric acid because of its powerful oxidizing action in hot solution. This action may become almost explosive in nature when very reactive reducing agents are being treated. With some organic compounds the action may be rather violent if proper care is not taken. Particular care must be exercised if the solution is evaporated until the acid fumes.

The correct procedure for using this acid is described in two monographs, "Perchloric Acid," and "Mixed Perchloric, Sulfuric and Phosphoric Acids and Their Applications in Analysis." These publications are available on request from the publisher, The G. Frederick Smith Chemical Co., 867 McKinley Ave., Columbus, Ohio.

a babbitt metal, containing tin, antimony, lead, and copper, dissolves directly in hot concentrated sulfuric acid. When the solution is diluted and cooled, lead sulfate precipitates and may be filtered off. In the Kjeldahl method for nitrogen (Exercise 25.11), digestion of the sample with concentrated sulfuric acid serves not only to dissolve a variety of nitrogen-bearing materials, but also to convert the nitrogen to ammonium sulfate. When the solution is made basic with sodium hydroxide, the ammonia may be volatilized out for measurement.

The following examples illustrate the use of mixed acids: (1) nitric and sulfuric acids in Drown's method for silicon in steel (Exercise 28.6); (2) sulfuric, nitric, and hydrochloric acids in the ASTM method for silicon in aluminum alloys; and (3) aqua regia for platinum metal alloys.

Treatment of a sample with an acid often may leave a residue that is insoluble in the acid. This acid-insoluble residue may be either some of the original material or a product of the original sample, that is, the result of a chemical reaction between the solvent and some sample component. Such a residue may be weighed and the result used analytically, as in low-silica limestones, or the residue may be subjected to further treatment to solubilize it.

Dissolution is necessary, not only for many samples at this stage, but often, in the course of an analysis, for many separated products. Various precipitates must be dissolved and then reprecipitated in order to be purified of contaminants; some precipitates are dissolved prior to titrimetric or colorimetric measurement; substances electrodeposited on platinum electrodes are dissolved therefrom, usually by acids. Many other examples of dissolution might be cited.

If the library assignment in Chapter 32 is an alloy, almost the first information needed is the names of possible solvents for each metal included in the alloy. A list that is very helpful for such an assignment is given in Lundell and Hoffman's brief survey of analytical problems.[2]

FUSION

If the solution attack is ineffectual in bringing about dissolution of the sample, high temperature treatment is usually necessary. Many substances, particularly rocks, ores, ceramic products, certain alloys, and others, cannot be dissolved satisfactorily until they have been fused with some compound or mixture. Such additives, known as *fluxes*, are usually substances that melt within the range of 150 to 750°, and that are sufficiently reactive chemically to attack the inert or resistant solid to be

[2] *Outlines of Methods of Chemical Analysis*, Wiley, 1938.

fused. In use, the flux is heated with the resistant solid until the flux fuses, that is, until it melts to a liquid. The liquid suspension thus obtained is maintained at an elevated temperature until as much of the solid substance as possible dissolves. With a silicate rock, for example, possibly an hour is required for all of the finely ground solid particles finally to disappear, giving a clear fused product for a sample of 0.5 g. The rate of reaction in such cases is very slow.

The flux selected depends upon the nature of the sample, but most often it is either acidic or basic in character, depending upon whether the substance to be fused is, respectively, basic or acidic.[3] Thus, siliceous materials are generally fused with sodium carbonate or a mixture of basic fluxes. Basic mixed oxides of iron and aluminum, in contrast, are fused with potassium pyrosulfate or a similar acidic flux. Typical fusion reactions are represented by the equations

$$CaSiO_3 + Na_2CO_3 \rightarrow Na_2SiO_3 + CaCO_3$$
$$Fe_2O_3 + 3\ K_2S_2O_7 \rightarrow Fe_2(SO_4)_3 + 3\ K_2SO_4$$

Problems are encountered in the selection of vessels of suitable material to withstand chemical action during such fusions. Metallic containers are generally most useful, with platinum leading the list on account of its resistance to many kinds of chemical action. Even platinum is not immune to attack, however, a detectable loss in the metal of the container resulting from each fusion involving sodium carbonate or potassium pyrosulfate. In fact, fusion with pyrosulfate if it is of long duration may remove enough platinum from a crucible to give a yellow chloroplatinate color when the mass is dissolved in hydrochloric acid. This color will interfere in the analysis if iron is to be determined colorimetrically as the yellow tetrachloroferrate ion, $FeCl_4^-$. Platinum ware should not be employed unless the analyst knows that its use is safe for the sample fused.[4]

Iron or, more often, nickel crucibles may be used for certain alkaline fusions in which any iron or nickel dissolved will not interfere with later separations or measurements. Low[5] recommended iron crucibles for fusing chromite ore (Exercise 26.7) with sodium peroxide, tin ores with sodium hydroxide, and sulfur or silica ores with sodium carbonate and sodium hydroxide. Nickel crucibles are recommended for fusions with sodium peroxide. The chief advantage of these two metals over

[3] For a brief, general discussion of the use of fluxes, see Hillebrand, Lundell, Bright, and Hoffman, *Applied Inorganic Analysis*, Wiley, 1953.

[4] See Chapter 28 for instructions on the use of platinum ware.

[5] *Notes on Technical Ore Analysis*, Wiley, 1923.

platinum is their lower cost. Sometimes pyrosulfate fusions are made in the porcelain or fused silica ware.

After fusions are completed and the mixtures are cooled, the residue is dissolved in a suitable solvent to obtain a solution for further manipulation. Occasionally, an insoluble portion is obtained which must be fused again. In some cases, an alkaline fusion is performed and the acidic portion of the sample is rendered soluble and is dissolved. The residue left then consists of the alkaline portion of the original sample. This residue is next subjected to fusion with an acidic flux to complete the solubilization of the material.

ADJUSTMENT OF CONDITIONS

Very often the conditions prevailing in a liquid sample, or in one suitably dissolved, are not satisfactory for the next operation. In addition, one separation may leave the system unsuitable for the next one until some readjustment is made. These adjustments are of several kinds, but most frequently they include changing the *p*H of the solution, buffering the solution at a fairly definite *p*H, changing the oxidation state of a constituent, and forming or eliminating complexes.

Many examples of these adjustments are scattered throughout the laboratory procedures described in subsequent chapters. In order to emphasize their importance, however, some typical applications are mentioned at this point, although their interpretation is considered in later chapters.

Control of pH

The *p*H of a solution is often very important for certain reactions. Thus, permanganate ion is generally used as an oxidant in very acidic solution, as in the determination of calcium (Exercise 26.4); but if this oxidant reacts with manganese (II) to precipitate manganese dioxide according to Volhard's method, the solution should be practically neutral. The titration of chloride ion with silver ion, with dichlorofluorescein as the indicator (Exercise 27.4), is not satisfactory unless the *p*H is that obtained by having excess solid calcium carbonate present. An example of the necessity for maintaining a strongly basic solution is found in the distillation step of the Kjeldahl method for nitrogen (Exercise 25.11).

Adjustment of *p*H is necessary both to make possible, and to prevent, various precipitation reactions. Hydrous ferric oxide precipitates with ammonia when the *p*H rises somewhat above 4; calcium ion and oxalate ion give calcium oxalate when the *p*H rises to about 6; as soon as mag-

nesium starts to precipitate, a large excess of ammonia is added to insure the formation of magnesium ammonium phosphate. All three of the above examples are discussed in the procedure for the analysis of limestone (Exercise 31.2).

In the determination of phosphorus in steel by the alkalimetric method, the sample is dissolved in nitric acid, and from this strongly acidic solution ammonium molybdophosphate, $(NH_4)_3[P(Mo_3O_{10})_4]$, is precipitated. Too much acid or too much hydroxyl ion prevents the formation of this well-known precipitate.

Silver chloride is precipitated in a solution slightly acidic with nitric acid to prevent the formation of silver carbonate or hydroxide (Exercise 28.3). Likewise, a solution barely acidic with hydrochloric acid prevents the precipitation of barium carbonate rather than, or along with, barium sulfate (Exercise 28.4). In each of these cases too much acid prevents complete precipitation of the desired constituent, presumably because of the formation of soluble complexes.

A related case is the separation of calcium and magnesium (Exercise 31.2), where enough ammonium chloride must be added, or formed in the solution, to prevent the precipitation of magnesium when the solution is made ammoniacal prior to the addition of ammonium oxalate to obtain calcium oxalate. One interpretation of this reaction is that the excess ammonium ion represses the ionization of the ammonium hydroxide to a point where there is insufficient hydroxyl ion concentration to precipitate magnesium hydroxide.

Adjusting a system to a specific *p*H, and then buffering the solution to hold the *p*H close to the chosen value, is a prerequisite for success in many processes. Examples are: (1) the titration of arsenic (III) ions with triiodide ion, in the presence of excess sodium hydrogen carbonate (Exercise 26.10); and (2) the titration of triiodide ion, liberated by copper (II) ion, with thiosulfate in the presence of ammonium acetate and acetic acid (Exercise 26.13).

Control of State of Oxidation

Like control of *p*H, maintenance of particular states of oxidation often enables the analyst to obtain desired, or prevent undesired, reactions. There are many examples of systems wherein the principal reaction involves oxidation or reduction, precipitation, or formation of a complex.

As examples of preliminary reduction or oxidation in titrimetry, reduction of iron (III) to iron (II) (Exercise 26.6), chromium (VI) to chromium (III) (Exercise 26.7), arsenic (V) to arsenic (III) (Exercise 26.10), and uranium (VI) to uranium (IV) (Exercise 26.8) is accom-

plished before titration back to the higher oxidation state with a suitable oxidant. In the case of uranium, any partial overreduction to uranium (III) must be counteracted by air oxidation back to uranium (IV).

In limestone analysis (Exercise 31.2) any iron should be in the ferric state to insure precipitation by ammonia. In contrast, chromium (III) is precipitated by ammonia, but chromium (VI) is not.

Arsenic is reduced to the tervalent state prior to distillation as arsenic (III) chloride (Exercise 26.10).

There are many examples of color-forming reactions wherein the desired colored system is formed only when a constituent is in a particular oxidation state. Thus, one must have iron (III) with ferron, iron (II) with 1,10-phenanthroline, nickel (IV) with dimethylglyoxime, copper (II) with diethyldithiocarbamate, chromium (VI) with diphenylcarbazide, uranium (VI) and titanium (IV) with hydrogen peroxide, arsenic (V) with ammonium molybdate (+ a subsequent reductant), vanadium (V) with phosphoric acid and sodium tungstate, and molybdenum (V) with thiocyanate (+ chlorostannous acid).

Complexation

The manipulation of constituents in the form of complexes constitutes a very important application of chemical reactions of particular types in order to facilitate subsequent separations and/or measurements. A few examples will illustrate the possible uses of complexation, decomplexation, and recomplexation. In general, such transformations are most often used to prevent interference by inactivating the potential interferers, and to make a constituent separable and/or measurable.

The use of complexes to avoid interfering reactions is common. A typical example is the addition of fluoride, phosphate, tartrate, or citrate to form colorless complexes with iron (III). In steel analysis, for instance, the iron is complexed with tartaric acid before the solution is made ammoniacal prior to precipitation of the nickel with dimethylglyoxime (Exercise 28.7). This complexant also prevents interference of such other metals as copper, cobalt, chromium, manganese, tungsten, and vanadium, if they are present in the steel.

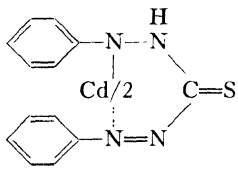
Iron complexed as fluoferrate (FeF_6^{-3}) will not react with iodide ion; otherwise it gives a positive error in the titrimetric determination of copper with thiosulfate (Exercise 26.13).

Many constituents are rendered separable, or at least the separation is facilitated, by the preliminary formation of certain complexes. For the electrolytic separation of silver, the metal should be in the form of the complex ion $Ag(CN)_2^-$, rather than the simple ion Ag^+, in order

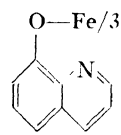
that a pure, adherent deposit may be obtained (Exercise 28.10). Iron will not deposit on platinum from an iron (III or II) solution, but it will from an oxalate complex. Perhaps the best method for separating cobalt is by the electrolytic method from an ammoniacal complex. Zinc will deposit from a solution in which it is complexed as zincate ZnO_2^-, but not from zinc (II) solution. Gold deposits in excellent physical state from the complex cyanide $Au(CN)_2^-$.

For separations by liquid-liquid extraction there is widespread application of complexes suitable for handling in this way with particular solvents. One of the best-known examples separable in this manner is iron in a solution strongly acidified with hydrochloric acid. Diethyl or diisopropyl ether is the usual extractant, and the complex involved is apparently the ion $FeCl_4^-$. The complex of iron (III) with thiocyanate is perhaps as well known, although interpretations of the formula range from $Fe(SCN)^{+2}$ to $Fe(SCN)_6^{-3}$.

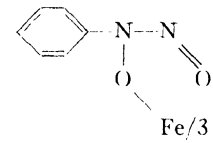
Many metal-chelate complexes, such as cadmium dithizonate (A), iron (III) oxinate (B), and iron (III) cupferrate (C), are extractable into solvents such as chloroform and carbon tetrachloride. Formulas for these three organometallic complexes are



(A)



(B)



(C)

This technic is particularly useful as a preparative-separative process prior to the colorimetric measurement of very small amounts of a number of such metals.

Although the preparative-separative processes just mentioned give a colorimetrically measurable system, more often the complexing step alone is used prior to colorimetric measurement. Such color-forming reactions are discussed in detail in Chapter 17.

Simple complexation is by far the most important type in colorimetric work. Recomplexation involves transforming one complex to another. Since it is more complicated, this approach is a sort of "last resort." Such a technic is exemplified by a method used for the determination of fluoride. In one variation an iron-thiocyanate solution of known color value is added to the fluoride-containing solution. The original colored solution fades to an extent proportional to the content of fluoride ion, as a result of the formation of colorless fluoferrate, FeF_6^{-3}.

CHAPTER 6

THE GENERAL PROBLEM OF SEPARATION

In the simplest kinds of quantitative analytical methods the analyst proceeds from the selection of the test sample directly to the measurement of the desired constituent. Such a case is the densimetric determination (specific gravity) of the antifreeze component in an automobile radiator solution. The majority of methods, however, require one or more intervening operations. Of the various operations, separation of the desired constituent is our present concern.

By "separation" is meant the physical removal from the system being analyzed of one or more components of this system. The component so removed may be (1) the desired constituent, (2) some derivative of this constituent, or (3) the interfering constituent(s). The frequent necessity of separation arises because of interference by some component(s) with subsequent measurement of the desired constituent.

The broad purpose of such separations, then, is to make the desired constituent measurable, either directly or indirectly. Whether the desired constituent is removed from the system in order to avoid interference, or whether the interfering constituent is removed, depends upon which process is easier to accomplish. For example, in water analysis all nonalkali metals are removed by precipitation before the remaining solution is finally evaporated to dryness preparatory to weighing of the resultant mixed sodium and potassium chlorides. In contrast, cyanide is distilled out of water and absorbed in a suitable solution for measurement.

Not only may the desired constituent or the interfering constituent(s) in the sample have to be separated, but also in many cases an excess of added reagent(s) must be removed. In brass analysis, for instance, the excess of nitric acid used in the dissolution step must be volatilized

out in order that satisfactory precipitation of lead as lead sulfate may subsequently be achieved.

The most difficult portion of the whole analytical procedure in many cases involves isolation of the desired constituent in a measurable state. The final operation, measuring the constituent, is usually simple. For example, in the determination of carbon in various kinds of materials, the isolation of carbon as the dioxide is the difficult step, rather than the measurement of the carbon dioxide formed. This measuring operation may be identical for widely different kinds of materials and separative processes. Thus, carbon in steel is converted to carbon dioxide by oxidation at high temperatures ($>1000°$), whereas the carbon in organic compounds is converted to carbon dioxide by a relatively low-temperature (approximately 600°) combustion process; limestone is treated at still lower temperatures (about 100°), with a strong acid, to liberate carbon dioxide; and carbon dioxide is removed from blood by the Van Slyke technic at room temperature. All four of these processes involve initial separation of the carbon as carbon dioxide by volatilization. Later, the carbon dioxide may be removed from the oxygen or air stream used by absorption in an alkaline solution or on solid soda-lime pellets preparatory to weighing. Other measuring possibilities are available, of course, for the product.

It may be mentioned, incidentally, that these preparative-separative processes and operations serve not only analytical but also production purposes. The general importance of isolation technics is emphasized by the following sentences which appeared in an article on the semi-annual report of the U.S. Atomic Energy Commission:

> Much of the chemist's work in the field of atomic energy comes under the deceptively simple heading, "Chemical Separation." The separation or extraction of one material from another, or more often from a mixture of others, had to be resolved in order to make the (atomic) bomb possible. Similarly, future progress is dependent upon more effective means of carrying out complex separations. In this work the chemists have studied all known methods of separation, including selective solvent extraction, distillation, precipitation, ion exchange, and liquid-liquid extraction.[1]

NATURE OF SEPARATION PROCESSES

Let us assume that the test sample has been subjected to any necessary preliminary treatment(s), as discussed in Chapter 5. Then the objective of any separation(s) necessary is to prepare a system in terms of which the desired constituent may be measured. Any operations pos-

[1] Atomic Energy Commission, *Chem. Eng. News* **28**, 538 (1950).

sible must be based upon the characteristic properties of the substances concerned. Thus, silver ion in aqueous solution may be precipitated by addition of chloride ion, since silver chloride, the product, is practically insoluble in water. Then the washed and dried precipitate may be weighed and the amount of silver calculated from the weight obtained. Nitric acid, however, would not serve as a precipitant for the silver ion, since silver nitrate is soluble in water.

The isolation of the desired constituent, or a substance related chemically to it, does not necessarily imply that the separated component contains *only* the desired constituent. The requirement is rather (1) that the component does not contain any source of interference with the subsequent measurement, or (2), that if there is such a source, the extent of its effect is determinable. An example of the first type of separation is the precipitation-separation of calcium as calcium oxalate. If the precipitate is to be converted by heating to calcium oxide for weighing, any excess ammonium oxalate used as washing medium for the precipitate is easily volatilized, and hence does not interfere with the weighing measurement. If the precipitate is dissolved in acid prior to titration of the oxalate ion with an oxidant, then any excess ammonium oxalate washing solution would be ruinous for the titrimetric measurement. An example of the second type of separation is the analysis of limestones in which an impure silica residue is often obtained. Correction for the mass of the impurity may be made by volatilizing the silica with hydrofluoric acid and considering the resultant loss in mass as the amount of pure silica.

In general, separations involve the differentiation and handling of solid, liquid, and gaseous phases of matter. Usually the system is a two-phase one, such as solid-liquid, liquid-liquid, or solid-gas. For example, solid silver chloride precipitates on contact with liquid water; gaseous carbon dioxide volatilizes from solid calcium carbonate; and the tetrachloroferrate ion, $FeCl_4^-$, extracts from liquid water into the immiscible liquid diethyl ether. Obviously, all of these cases involve heterogeneous equilibria.[2]

The extensive development in the last decade or two of analytical technics based on heterogeneous equilibria has been, largely, the result of need for more exacting analysis of complex mixtures, and, therefore, of need for better methods of separation.

Such processes involving heterogeneous equilibria are of importance not only to analytical chemistry, but also to chemical engineering. Analytical separations may be based upon chemical engineering processes,

[2] Elving, *Anal. Chem.* **23**, 1202 (1951).

such as counter-current extraction; conversely, production processes may be based upon analytical technics. Synthetic organic chemistry is dependent to a great extent upon the ability of the investigator to separate mixtures resulting from his syntheses. Furthermore, it is necessary in many cases to determine the purity or homogeneity of each fraction separated, and to identify the pure compounds formed.

In recent years a number of significant additions and modifications have been made to available separation processes. Generally the newer technics serve the same purpose as the older ones, such as precipitation. Thus, aromatic hydrocarbons can be removed from a mixture of aromatic, paraffinic, and naphthenic hydrocarbons by differential adsorption upon silica gel; or a C_4-fraction of hydrocarbons suitable for a determination of butadiene can be secured by fractional distillation. Subsequent chapters elaborate upon such processes.

CLASSIFICATION OF SEPARATION PROCESSES

To classify methods of separation on the basis of the physical and chemical properties of the constituents of materials is difficult. Therefore we have no such classification at the present time. As a broad basis of differentiation one may speak of "mechanical" and "chemical" methods of separation. "Mechanical" refers to those separations that are made without changing the state of, or bringing about a chemical reaction with, the constituents of the sample. Examples of mechanical separation include the separation by filtration of suspended matter in gases and liquids, the manual or magnetic removal of constituents from samples, and the sieving analysis of heterogeneous materials, such as gravel, into particles of different sizes. "Chemical" refers to separation processes involving either a transformation, such as a change in state or condition, or a reaction resulting in a change in status. The chemical group includes the great majority of separations used in analysis. Familiar examples are the precipitation separation of barium sulfate and the volatilization separation of the water of crystallization of barium chloride dihydrate.

In many cases, separation is performed with the aim of producing a substance in a state as nearly pure as possible. The substance may be an element, a compound of two or more elements, an ionized radical (in the mass spectrograph), or a mixture of two or more compounds. An example of the last possibility is found in the separation of ethanol from alcoholic liquors by distillation. The distillate contains all of the alcohol, together with considerable water; but the composition of this binary mixture is readily determined, after dilution to a definite

volume with more water, by measurement of a physical property of the solution, such as specific gravity. Precipitation or electrodeposition are widely used for the separation of elements or of compounds of two or more elements, usually for the desired constituent itself.

From a general viewpoint, separations may be considered in terms of the phase transformation involved in the process. These phases refer, of course, to the three familiar states of matter, solid, liquid, and gas. In theory, at least, all the phases listed in Table 6.1[3] are possible. Definition of the terms used in Table 6.1 and discussion of the relevancy of the examples listed are reserved for subsequent chapters.

Cassidy[4] has summarized the bases of some methods of separation, and of tests for purity, from the viewpoint of partition between phases.

TABLE 6.1

TYPES OF SEPARABLE SYSTEMS

Phases Involved	*Processes*	*Examples* *Constituent (from)*
1. Solid-solid	Sieving	C (cast iron)
	Magnetic action	Fe (nonmagnetic matter)
2. Solid-liquid	Precipitation	Se (solution)
	Electrodeposition	Cu on Pt (solution)
	Adsorption	
	General	$BaSO_4 + Fe^{+++}$ (solution)
	Differential	
	No exchange	Chlorophylls (solution)
	Ion exchange	Na^+ on Dowex 50 (solution)
3. Solid-gas	Condensation	Ice (water vapor and air)
	Adsorption	H_2 on Pd (air)
4. Liquid-solid	Dissolution	Sucrose (sand)
5. Liquid-liquid	Distillation	Fractions (petroleum)
	Extraction	$UO_2(NO_3)_2$ (interferers)
	Electrodeposition	Fe^{+++} in Hg cathode (UO_2^{++})
6. Liquid-gas	Condensation	Hg (air)
	Absorption	CO_2 in KOH (air)
7. Gas-solid	Volatilization	H_2O ($BaCl_2 \cdot 2\ H_2O$)
8. Gas-liquid	Volatilization	NH_3 (aqueous solution)
9. Gases	Diffusion	$U^{235}F_6$ ($U^{238}F_6$)
	Magnetic action	Ions (those having different ratio of mass to charge)

IMPORTANT SEPARATION PROCESSES

Some of the most widely used methods of effecting separations are considered in the four succeeding chapters; the specific processes are

[3] Mellon, *Anal. Chem.* **22**, 1342 (1950).
[4] *J. Chem. Educ.* **23**, 427 (1946).

volatilization, precipitation, electrodeposition, and *partition.* Of the different factors entering into the application of each method, the following are probably of most importance: the nature of the process, including the means of separation employed; the nature and disposal of the products; and the applicability and merits of the method. In these chapters only distinctive general principles are presented, together with some reference to specific details in illustrative procedures. Examples of the actual application of different methods of separation are included in the laboratory exercises described in Chapters 25 to 31.

For some constituents the analyst has no choice of the method he will use in a given situation; for others, he may have a choice. The situation depends upon the specific nature of the constituent to be separated and of the other constituents in the system, and also upon the nature of the final measuring operation to be used.

If there is a choice of separation method, the analyst's decision should be based upon a consideration of the merits and the limitations of the possible methods. Factors such as the following are concerned: (1) the time, skill, and attention required to obtain the requisite degree of accuracy; (2) the efficiency of the separation; (3) the general and special applicability of the method; (4) the cost of chemicals, apparatus, and laboratory services; and (5) the availability of special services.

CHAPTER 7

SEPARATION BY VOLATILIZATION PROCESSES

The calcinations, combustions, distillations, and sublimations of the alchemists constitute one approach which analysts have long used to make separations. Such processes are based ultimately upon the different volatilities of different substances.[1]

To carry out these processes requires primarily that the temperature of the test sample be controlled in a manner such that there is an adequate difference in the vapor pressure of the components to be separated. In addition, certain prior or accompanying preparative treatment is often necessary to render a given component separable.

Based upon the degree of complexity of the process, one may distinguish between simple and fractional volatilization. A brief description of each type follows.

SIMPLE VOLATILIZATION

Essentially, all methods of simple volatilization are based upon heating the sample, with or without added reagents, and without recycling part of the volatilized product(s). Thus, many kinds of solid samples that are wet with water may be dried simply by heating for a sufficient length of time at a temperature high enough to volatilize the water; or, to give an example of a liquid sample, the carbon dioxide dissolved in distilled water may be eliminated by boiling the water a short time.

These methods are applied to systems in the solid or liquid state,

[1] Before discussing this chapter with his students, the instructor may wish to review the fundamental factors involving vapor and dissociation pressure. The extent of the material to be covered, and its application to volatilization separations, will depend upon the background of the students and the time available. The theory of distillation, in its varied applications, is an extensive and complicated subject.

the phase transformation being from a solid or liquid to a gas. Blasdale's gas-evolution methods[2] have this principle as their distinctive feature.

Examples of Simple Volatilizations

Perhaps the simplest type of volatilization involves merely a change in state of the component separated. An excellent example is the determination of adsorbed moisture held on the surface of many substances. Thus, finely ground iron ores, stored at room temperature, have an appreciable percentage of water so held. Some wet coals have more than 10 per cent of moisture. The procedure of analysis for the adsorbed moisture depends upon regulation of the environmental conditions so that the vapor pressure of the water will be sufficiently high to cause all of this component to change its state fairly rapidly from a liquid to a gas, and to be evolved from the system. Comparable changes of state occur in many determinations in which the term "evaporation," or "sublimation," is applied to the process.

In order to insure that only the component wanted is evolved, the operating conditions may have to be carefully controlled. In coal analysis, for instance, the procedure for determination of moisture calls for strict regulation of temperature in a particular type of ventilated oven, since, of the many volatile constituents in coal, only the water is desired.

Some substances, such as grains, are heated in the presence of an immiscible liquid, such as toluene, in order that only the water is evolved. The water and immiscible toluene distill off together and collect in two layers, where the water may be measured.[3] An analogous procedure is the determination of water in petroleum products, with the use of petroleum naphtha as the immiscible liquid.[4]

Dissociation of a substance to give one or more volatile components represents a slightly different case. Thus, barium chloride dihydrate, $BaCl_2 \cdot 2\ H_2O$, may have a film of moisture on each individual particle, in addition to the water of crystallization. Careful drying, at a sufficiently low temperature, will evolve this adsorbed moisture. To evolve the water of crystallization the material is heated just below redness (see Table 7.1, page 81), according to the instructions given in Exercise 28.1. The material dissociates according to the equation

$$BaCl_2 \cdot 2\ H_2O \rightleftarrows BaCl_2 + 2\ H_2O \uparrow$$

Long heating at much higher temperatures will evolve chlorine from the anhydrous barium chloride, with the resultant formation of barium

[2] Blasdale, *Fundamentals of Quantitative Analysis*, p. 79, Van Nostrand, 1936.
[3] Association of Official Agricultural Chemists, *Methods of Analysis*, p. 342, 1950.
[4] Am. Soc. Testing Materials, *ASTM Standards 1952*, Part 5, p 45.

oxide from oxygen in the air. The reaction is

$$2\ BaCl_2 + O_2 \rightarrow 2\ BaO + 2\ Cl_2\uparrow$$

The determination of "loss on ignition" of limestone is another example in which heating, in an open crucible, serves both to dissociate the volatile component and to evolve it from the system. The dissociation is expressed by the equation

$$CaCO_3 \rightleftarrows CaO + CO_2\uparrow$$

For this reaction to proceed with reasonable speed, the temperature should be approximately 900°. It should be pointed out, of course, that limestone often contains components other than carbon dioxide that may be volatilized at 900°. However, the value for "loss on ignition" may be a close enough measure for various industrial evaluations of the quality of the stone (Exercise 31.2).

Limestone may be taken also as an example to illustrate the use of an added reagent to facilitate the liberation of a component to be volatilized. Thus, in the procedure described in Exercise 28.2 a strong acid is added to the evolution flask containing the sample. With perchloric acid, the reaction is

$$CaCO_3 + 2\ HClO_4 \rightarrow Ca^{+2} + 2\ ClO_4^- + H_2O + CO_2\uparrow$$

When the solution is boiled gently, the carbon dioxide is volatilized out of the evolution flask; any water vapor carried out simultaneously must be absorbed if the carbon dioxide is to be caught and weighed.

Where more than one volatile component is present, mere regulation of the temperature of heating may suffice to control desired reactions, as, for example, with coals and barium chloride dihydrate. Temperature regulation alone may not be adequate, however, at least without somewhat elaborate equipment. Thus, copper sulfate pentahydrate, $CuSO_4 \cdot 5\ H_2O$, gives up four of the water molecules rather easily

$$Cu(H_2O)_4SO_4 \cdot H_2O \rightarrow CuSO_4 \cdot H_2O + 4\ H_2O\uparrow$$

The fifth water molecule is evolved only on reaching a temperature high enough for some sulfur trioxide to evolve

$$CuSO_4 \cdot H_2O \rightarrow CuO + SO_3\uparrow + H_2O\uparrow$$

To obtain the fifth molecule without this loss of sulfur trioxide, the analyst may heat the material with sodium tungstate, which is nonvolatile at the temperature used. The reaction then proceeds according to the equation

$$Cu(H_2O)_4SO_4 \cdot H_2O + nNa_2WO_4 \rightarrow Na_2SO_4 + CuO + WO_3 + (n-1)Na_2WO_4 + 5\ H_2O\uparrow$$

Still another instance of the use of a liberation reaction prior to volatilization occurs in the analysis of brass (Exercise 31.3). Here sulfuric acid is added to the solution containing lead, copper, and zinc nitrates, and the whole is evaporated to fumes of sulfur trioxide in order to expel the nitrate ion as volatile nitric acid. This leaves the metals in the residue as sulfates. The addition of the sulfuric acid does not change the volatility of any constituent present; rather, as a high-boiling liquid, it maintains a solution during the removal of the nitric acid.

Carbon may be separated in the analysis of cast iron and steel by burning the sample in a stream of oxygen at 1000 to 1200°. The carbon dioxide, formed according to the reactions

$$C + O_2 \rightarrow CO_2\uparrow$$
$$4\ Fe_3C + 13\ O_2 \rightarrow 6\ Fe_2O_3 + 4\ CO_2\uparrow$$

is volatile at this temperature and is swept along by the excess oxygen for suitable processing before measurement.

In organic chemistry the determination of carbon and hydrogen in a substance by combustion of the sample in a stream of oxygen is a classical method. In analysis of sucrose, for example, the carbon burns to carbon dioxide and the hydrogen to water, the equation being

$$C_{12}H_{22}O_{11} + 12\ O_2 \rightarrow 12\ CO_2\uparrow + 11\ H_2O\uparrow$$

The products formed may be weighed after absorption of the water in calcium chloride and the carbon dioxide in soda lime.

One of the best-known analytical methods is that of Kjeldahl for determining nitrogen in a variety of organic and inorganic materials. Preliminary digestion of an organic compound, for example, with sulfuric acid converts the nitrogen to ammonium sulfate

$$\text{N-compound} + H_2SO_4 \rightarrow (NH_4)_2SO_4 + \cdots$$

When the resulting mixture is made alkaline, the nitrogen is liberated as ammonia

$$(NH_4)_2SO_4 + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O + 2\ NH_3\uparrow$$

which is then evolved by distillation and caught in a suitable apparatus (Exercise 25.11).

Equilibria Involved

In order to demonstrate the function of equilibria in one simple volatilization process, the ignition of limestone to constant weight (Exercise 31.2) to obtain the loss on ignition may be used as an example.

The dominant reaction at 900° is represented by the equation

$$CaCO_3 \rightleftarrows CaO + CO_2 \uparrow$$

On applying the mass law, we have the expression

$$\frac{[CaO] \times [CO_2]}{[CaCO_3]} = K$$

In a gaseous mixture the concentration of a gas is proportional to the partial pressure it exerts. It is most convenient, therefore, to express the concentrations in the equilibrium equation in terms of their partial pressures, and the equilibrium constant K in units of pressure, e.g., millimeters of mercury.

Since the solids, calcium oxide and calcium carbonate, have very small vapor pressures at 900°, their concentrations may be taken as constant and will cancel. Thus, the equilibrium expression becomes

$$K = [CO_2] = p_{CO_2}$$

The value of K varies with temperature, but is constant at any given temperature. Thus, no appreciable decomposition will take place until the partial pressure of the carbon dioxide in the sample exceeds that of the carbon dioxide in the atmosphere to which the sample is exposed.

Reference should be made to elementary textbooks of physical chemistry for a discussion of the general theory of simple volatilization separations as applied to liquids. This discussion includes the nature and use of steam distillation.

Equipment

From the previous discussion, it is evident that any special equipment for the evolution process consists principally of apparatus for producing and maintaining desired temperatures, together with any apparatus needed for accomplishing the process and handling the product(s). The requirements in specific cases depend upon the properties of the constituents concerned. In a few limited cases of separation by volatilization, mere exposure to the atmosphere at room temperature is sufficient, as for the evaporation of diethyl ether, which boils at 34.6°. Very low-boiling liquids, encountered in some kinds of gas analysis, may vaporize far below room temperature. In the great majority of cases, however, some means must be employed to raise the temperature of the sample above that of the laboratory. Depending upon the temperature sought, one may consider these means under three roughly defined groups: ovens and furnaces, burners, and stills.

Ovens and furnaces. For the elimination of certain solvents, or the

removal of moisture from such samples as iron ore, many substances are dried at a temperature somewhat above 100° (most often the range is 105 to 110°). For this purpose electric ovens, such as that illustrated in Figure 7.1 are widely used. In general, electric ovens should be used only for removing noncorrosive components from solids.

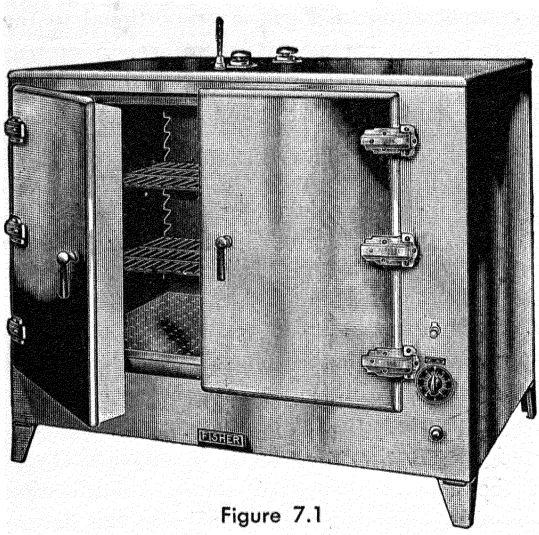


Figure 7.1
Electric drying oven (courtesy Fisher Scientific Co.).

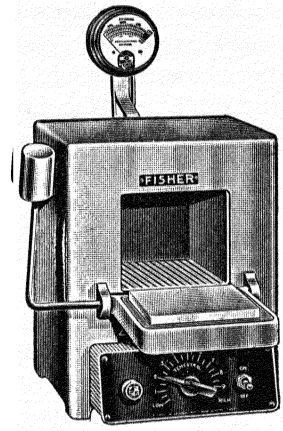


Figure 7.2
Electric muffle furnace (courtesy Fisher Scientific Co.).

Solutions should be evaporated by means of open steam baths and by high-pressure steam, gas, and electric hot plates. Such evaporation of solutions may be facilitated in certain cases by directing a stream of dry, hot air across the surface of the solution being heated. Suspension of an electric heating unit, such as an infrared lamp, above the surface of the solution is also advantageous. Use of either of these procedures avoids the difficulty encountered when the solution contains a solid residue and is inclined to "bump."

The term "drying" is much used to refer to the process taking place in the volatilization of a product from a solid within the temperature range slightly above the boiling point of water. For temperatures considerably above those employed in drying, the term "ignition" is generally applicable, although the lower limit to which it applies is not very definite. There are a number of procedures requiring ignition of a product in the general range of 200 to 600°, examples being lead dioxide at 230°, stannic oxide with ammonium iodide at 450°, and lead

sulfate at 600°. Electric furnaces or muffles, as shown in Figure 7.2, suitably regulated, can be conveniently used for temperatures up to 1000° or even higher. An important advantage of such furnaces is their ability to maintain a relatively constant temperature, a necessity in some procedures. An example is the conversion of calcium oxalate to the carbonate, as described in Exercise 28.5 for the determination of calcium.

Often, simpler and less expensive equipment must suffice. Small flasks may be partially covered in a sand bath, in which a thermometer

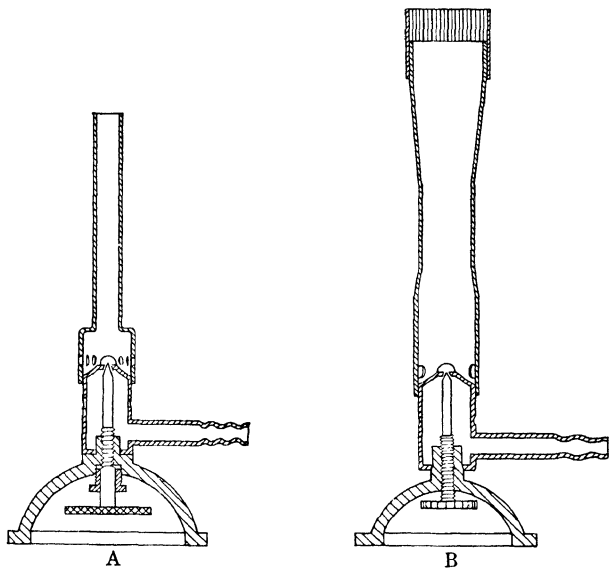


Figure 7.3

Tirrill (A) and Meker (B) types of burners.

is placed, and under which there is a burner with a flame of suitable intensity. The temperature of 600° required for lead sulfate may be approximated by suspending the Gooch crucible, containing the precipitate, inside a larger crucible by means of a ring of asbestos board placed inside the larger crucible and containing a hole to hold the smaller crucible. The large crucible is then heated to low redness with a Bunsen burner.

Burners. To attain ignition temperatures of 800 to 1200° on the laboratory desk vigorous heating is necessary. For many years gas burners have been the common equipment used for this purpose. Figure 7.3 illustrates two types of burners widely used for the lower ranges.

Figure 7.3A shows the Tirrill type of Bunsen burner. When burning at maximum efficiency on artificial gas, the burner reaches a temperature probably in the neighborhood of 850 to 900°. Figure 7.3B shows the Meker type of burner. The grid in the top causes many small cones to form in the flame. Close to the tip of these cones the maximum temperature may be 50 to 100° higher than with the Tirrill burner. With the larger Meker burners the flame so envelops small objects that the operator may encounter difficulty in maintaining good oxidizing conditions in the center of the flame. Consequently, unless care is taken, some reduction may occur during heating of a precipitate such as barium sulfate. There is also a blast-type of Meker burner, in which compressed air or oxygen can be delivered into the center of the burning flame. Figure 7.4 shows in cross section the common design of the blast lamp. In the blast lamp a stream of air, air and oxygen, or oxygen alone is blown into the center of the gas flame. Under optimum conditions the temperature may approach 1200°, a condition needed to complete the dehydration of some products, such as aluminum trioxide. The noise of most types of blast lamps is objectionable, especially if many of them are operating simultaneously.

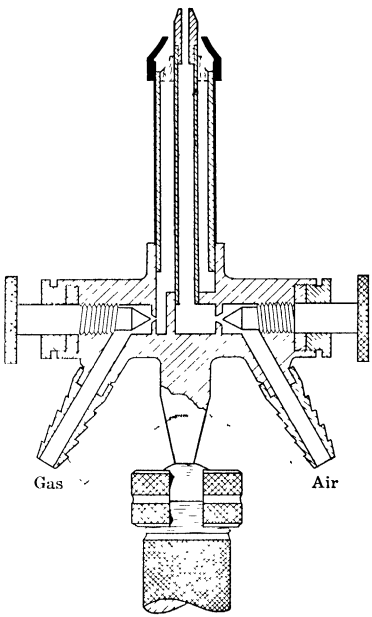


Figure 7.4

Cross section of a blast lamp.

It is important for the student to remember that, while the outside of a crucible may be heated by the burner to redness,[5] indicating a temperature of about 700°, the inside of the crucible and its contents

[5] A common direction in laboratory procedures is to heat an object, such as a crucible, to a temperature indicated by the color of the object. For example, the directions for igniting lead sulfate may call for heating the crucible to a dull red heat. Table 7.1 gives the approximate temperatures associated with the various colors of hot objects. Strictly speaking, this color scale of temperatures is based on the appearance of a black body at various temperatures. However, the difference in color of black bodies and other bodies is negligible in the higher temperature ranges. Naturally, the color observed is dependent on the keenness of eyesight and color perception of the observer and upon the illumination level in the laboratory. In general, however, the temperatures listed in Table 7.1 do apply for the colors given, as observed by a person with normal eyesight in a normal laboratory where the object observed is not in direct sunlight.

may be 50 to 100° cooler as a result of the loss of heat by radiation. Covering the crucible with a lid helps to minimize heat loss and to keep the inside temperature closer to that of the outside. Heating the crucible in an electric muffle furnace insures that both the crucible and its contents are at the desired temperature.

TABLE 7.1

COLOR SCALE OF TEMPERATURE

Color Observed	*Temperature* (in °C)
Lowest red, visible in the dark	470
Dark red	550
Dark cherry	625
Cherry-red	700
Light red	850
Orange	900
Light orange	950
Yellow	1000
Light yellow	1050
White	1150-1200
Bright white	1400
Dazzling white	1500-1600

Stills. A useful distinction, at least in terms of their separative effectiveness, may be made between what may be called simple stills and fractionating stills.

Simple stills are represented by the apparatus shown in cross-section in Figure 25.2 (page 418) and in Figure 26.2 (page 440). Both of these examples illustrate assemblies for the volatilization of a desired constituent, along with some solvent, by simple heating of the solution.

Figure 25.2 illustrates familiar equipment arranged for distillation of ammonia from an alkaline solution, according to the well-known method of Kjeldahl. On boiling of the solution in the distillation flask, the ammonia, as well as some water, is volatilized over into the condenser at the lower end of which the condensate containing the ammonia is collected. Figure 26.2 shows a side-arm distillation flask connected to a Liebig-type condenser. This setup is designed for the volatilization of arsenic (III) chloride by boiling a solution of Paris green in a reducing environment. The aqueous condensate is collected in a receiver arranged to keep the arsenic in the reduced state subsequent to titration with an oxidant.

More complicated stills are discussed later in this chapter.

FRACTIONATION VOLATILIZATION

The principle of fractionation can be applied to render certain volatilization technics increasingly efficient by a stepwise or continuous repetition of the separation process through the countercurrent flow of phases. Such an arrangement takes advantage of the degree of completeness of transfer of the desired constituent that is possible. A countercurrent fractionation process involves two phases, e.g., liquid and gas, moving in opposite directions and having similar concentration gradients in reference to the constituent being transferred between the two phases.

One method of obtaining added efficiency of separation by means of countercurrent contact is by the use of refluxation. In this way part of the product is returned to the system for further transfer of material out of the returned phase. A familiar example of the use of the reflux principle is in rectification or fractional distillation in which the complementary processes of vaporization (volatilization) and condensation alternate. The ascending vapor (gaseous phase) is transformed by a process of heat exchange into a phase (gaseous) which is enriched in the more volatile desired components, and a condensed phase (liquid) which is richer in the undesired higher-boiling components. The complementary process occurs via the same process of heat exchange for the descending reflux stream of liquid.

Distillation

The use of distillation as a means of separating inorganic materials has not had general application because of the relatively low vapor pressure of nearly all inorganic compounds at temperatures below 250°. However, there are a few very important separations that depend upon distillation. The Scherer procedure (Chapter 31, Special Brasses) for the determination of arsenic, antimony, and tin in nonferrous alloys depends upon the selective separation by distillation of compounds of these three elements.

Distillation is one of the most important methods of separating liquid organic compounds. The process is often called "fractional" distillation in order to emphasize its separative function. In organic preparative work fractional distillation has long been used as a means of separation; refining processes in the petroleum industry represent its most spectacular industrial application.

The use of distillation as a general means of separation in analytical chemistry has come into prominence only in the last two decades, largely because of the development of efficient apparatus by Fenske, Podbielniak,

and others. In the following discussion the fundamental features of analytical laboratory distillation are summarized.

Apparatus

The three fundamental parts of a fractional distillation apparatus—stillpot, column, and stillhead—are illustrated in Figure 7.5. The stillpot, which contains the sample to be distilled, is heated by external or internal heating units. Space is provided for the vapor formed to separate from the liquid sample. The column is usually a tube surrounded by some device (usually an air, vacuum, or insulation jacket) for preventing loss of heat from the column and its contents to the surroundings. In addition, for the distillation of either very low- or

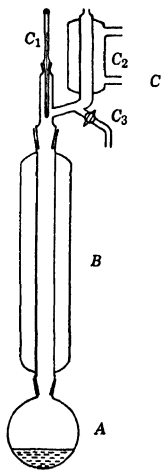


Figure 7.5

Essential parts of apparatus for fractional distillation. *A*, stillpot, which is usually a bell-shaped or cylindrical container; *B*, column, which is, as a rule, 12 to 60 in. long and 0.25 to 2.0 in. in diameter; *C*, stillhead; C_1, thermometer; C_2, condenser; C_3, apparatus for withdrawing part of condensate and returning part as reflux.

very high-boiling samples, arrangements may be made for cooling or heating the column. In order to insure intimate contact between the rising vapors and the descending reflux (explained in the next section) and to provide for the separation of entrained droplets of liquid from the ascending vapors, the column is "packed" or provided with suitable devices which will fill the space. These devices include such substances as very small cylinders, helices, and rings, made of glass, ceramic ware, or pierced plates, spirals, gauze, and woven shapes, made of metal.

The stillhead consists of three essential parts: (1) a thermometer or other device for measuring the temperature of the vapor leaving the column immediately prior to condensation; (2) a condenser for converting the vapor taken from the column back to a liquid; and (3) an

apparatus for withdrawing from the still part of the condensate thus formed and returning part to the column as reflux.

Operation. Whenever a mixture of two miscible liquids is heated, the vapor evolved will usually contain a greater percentage of the lower-boiling component than was present in the original liquid mixture. If the vapor is removed and cooled until entirely condensed, the condensate formed will be relatively richer in the lower-boiling component, and the

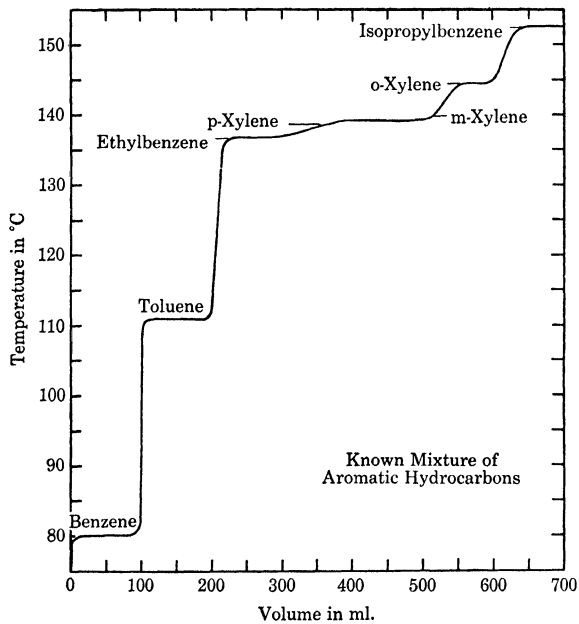


Figure 7.6

Plot of the boiling point as a function of volume for the distillation at 770 mm of the aromatic hydrocarbons from a known test mixture [reproduced with permission from Rossini *et al., Proc. Am. Petroleum Inst.* **23**, sect. III, 7 (1942)].

liquid left in the stillpot will be relatively richer in the higher-boiling component. This operation suffices only for the separation of liquids of widely different boiling points.

When the vapor evolved from a two-component system is only slightly cooled, it is only partly condensed. The resulting condensate is relatively richer in the higher-boiling component, and the remaining vapor is relatively richer in the lower-boiling component. The latter vapor can, in turn, be partially condensed to give a vapor still richer in the lower-

boiling component. The fractionating column is a device which provides a means for operating a series of the latter type of processes in an efficient manner. The combination of the stillhead and column constitutes the most efficient scheme for separation by distillation. This reflux principle is known as "rectification."

In this reflux process which occurs in the stillhead, the refluxate[6] flows down the column and is brought by the packing material into intimate contact with the rising vapors. This contact results in an exchange of heat and material. Part of the less volatile component in

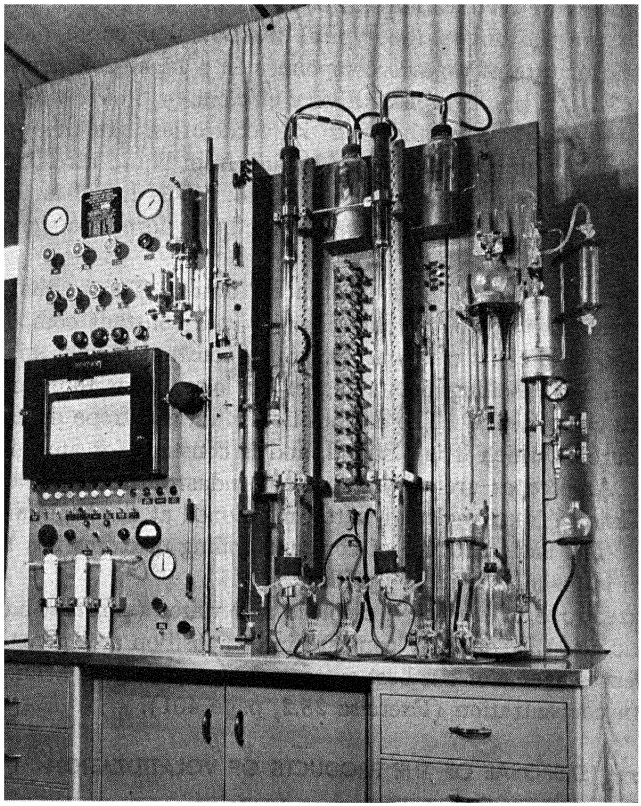


Figure 7.7

View of automatic "Hyd-Robot" low-temperature, recording fractional distillation apparatus (courtesy Podbielniak, Inc.).

[6] This new word is used to designate the partially separated condensate returned to the place of volatilization in the column.

the vapor is condensed by the removal of heat by the refluxate. Absorption of this heat by the refluxate causes vaporization of its more volatile component, thus making the vapor still richer in the lower-boiling component.

Continuous repetition in the column of the process just described, together with the return as refluxate of most of the original material condensed in the stillhead, results even in the separation of liquids which boil within a few degrees of each other. In general, in separation of a pair of liquids, the closer the boiling points are, the greater the length of column and the greater the reflux ratio[7] necessary.

The process of rectification is not restricted to two-component mixtures. Figure 7.6 shows the typical fractionation curve obtained on distilling a mixture of organic compounds in a high-efficiency still.

Figure 7.7 is a photograph of a very efficient type of low-temperature distillation apparatus, together with its accessories. In this apparatus, gas samples containing components boiling from liquid air temperatures up to about 35° are condensed to a liquid. This liquid is then automatically distilled and the data are recorded in a form analogous to that shown in Figure 7.6.

Occasionally, two or more substances form a mixture that, despite efficient rectification, boils or distills over in a constant composition as regards the ratio of its components. Such constant boiling mixtures, or *azeotropes,* have boiling points higher or lower than those of any of their pure components. The composition of an azeotrope depends upon the pressure at which it is distilled, and is constant for any given temperature. Azeotropes are very important industrially and analytically; the best-known is ethanol and water, mentioned at the beginning of the chapter. The basis and use of constant boiling mixtures has been well discussed in a simple manner by Fleer.[8]

The azeotrope of hydrogen chloride and water (constant-boiling hydrochloric acid) is so nearly constant in composition at a given pressure that it serves as one of our best systems for preparing an acidic solution of known concentration (Exercise 25.2, page 401).

DISPOSAL OF THE PRODUCTS OF VOLATILIZATION

Since the purpose of the present chapter is to treat the process of volatilization, we are not directly concerned with what becomes of the

[7] The reflux ratio is here defined as the ratio of the quantity of the refluxate returned to the quantity of product withdrawn. Reflux ratios of from 20 to 1 up to 100 to 1 are commonly used in analytical distillations.

[8] *J. Chem. Educ.* **22,** 588 (1945).

constituent volatilized. Actually, of course, separations are merely incidental to the preparation of some product for measurement. The methods of measurement are treated later; here it will suffice to indicate certain types of disposition which may be made of the products.

The volatile product is either eliminated from the system and disregarded, or is collected in some way and measured. In the former case, the residue is measured. This residue may be the desired constituent, or a product definitely related to it. The ash in coal, for example, is determined by burning out all volatile matter and weighing the residue. Or the residue may not be the desired product, but may contain everything except the desired constituent, which has been expelled. Thus, in determining water in barium chloride dihydrate, water is the component sought; but the anhydrous salt remaining is weighed and the loss is then assumed to be water of crystallization.

If the residue is not measured, the volatile product is collected and measured. One or more of the different kinds of methods outlined in Chapter 11 may be applied, the method selected depending on the nature of the constituent, and the various other factors mentioned in Chapter 11. As an example of the principles of some of the methods, for collecting and measuring volatile products, the determination of carbon dioxide volatilized from a solution of pure sodium carbonate may be taken. An estimation of the amount of gas evolved by a reagent acting on the carbonate may be made by any of the following methods: *volumetrically,* by purifying the gas and measuring its volume at a known pressure and temperature; *manometrically,* by purifying the gas and measuring its pressure at a known volume and temperature; *titrimetrically,* by absorbing the gas in excess standard solution of barium hydroxide and back titrating with acid; *gravimetrically,* by evaporating a measured amount of solution to dryness with excess sulfuric acid and weighing the residue of sodium sulfate, by absorbing the gas in a liquid or solid absorbent and weighing it directly, or by absorbing it in barium hydroxide solution and weighing the precipitated barium carbonate; and by certain other methods, such as the determination of the electrical conductivity of a solution of barium hydroxide before and after the absorption of the carbon dioxide.

In the fractional distillation of organic compounds, the fraction obtained at a given temperature may be weighed or its volume measured; the latter is conveniently done by catching the distillate in a calibrated receiver such as a graduated cylinder. The results are then expressed, respectively, as weight or volume per cent of the sample added to the stillpot. In the Podbielniak apparatus, illustrated in Figure 7.7, the

constituents distilled are caught in containers of fixed volume and the resulting pressure automatically recorded. A distillation curve similar to that in Figure 7.6 is obtained.

APPLICATIONS OF VOLATILIZATION

Specific examples have already been cited to indicate the general nature of the situations in which separation by volatilization may be employed. An examination of the procedures of analysis in reference works shows that volatilization methods of separation are specified in a large number of cases.[9] It is not unlikely that a count would reveal that the method is applied more frequently than any other process of separation; its most serious competitor would be the precipitation method.

For some substances in the gaseous state, one should be able, theoretically at least, to separate the components by what amounts to a reversal of the process of volatilization, that is, by fractional condensation. In practice, however, the manipulative difficulties are such that analysts generally have preferred to cool the whole sample to a low temperature and then to make the required separations by fractional distillation.

The application of separation by fractional distillation is well known for its versatility and efficiency. Especially in the petroleum industry it has become a powerful analytical tool, both for the separation of fractions for measurement and for analysis *per se*. The process has been discussed in detail by Rose.[10] It is pertinent to mention that fractional distillation was the first example of an analytical separation process to be instrumented for fully automatic operation, by the well-known Podbielniak apparatus (Figure 7.7).

More emphasis should be placed on the possible applicability of fractional distillation to inorganic systems. The use of the Scherer method [11] for separating arsenic, antimony, and tin by distillation from hydrochloric acid solution is well known and is standard in nonferrous alloy analysis. The separations in this method are probably azeotropic in nature, constant-boiling mixtures being formed between the metal halide or the polyhalometal acid and the halogen acid. Another example of use of this technic for inorganic systems is the separation of ger-

[9] See, for example, Carney, *Laboratory Fractional Distillation,* Macmillan, 1949; Robinson and Gilliland, *The Elements of Fractional Distillation,* McGraw-Hill, 1950; Rose, *Anal. Chem* **21,** 81 (1949), **22,** 59 (1950), **23,** 38 (1951), **24,** 60 (1952), **25,** 101 (1953); Rose, "Distillation" in Weissberger, ed., *Technique of Organic Chemistry,* Vol. IV, Interscience, 1950; and Ward, *U.S. Bur. Mines, Tech. Paper* **600** (1939), "Review of the Literature on the Construction, Testing, and Operation of Laboratory Fractionating Columns."

[10] *Anal. Chem* **22,** 1368 (1950).

[11] *J. Research Nat. Bur. Standards* **16,** 253 (1936).

manium by distillation of the tetrachloride. Other cases are known, but it seems worthwhile to investigate further use of the volatility of metallic compounds in the analysis of inorganic materials. Use of halogen, carbonyl, and organic *beta*-carbonyl compounds seem to be possibilities in separating the transition elements.

Certain specific advantages may be recognized in volatilization methods. The desired constituent is often handled as a gas and is frequently purified and eliminated with ease. Under controlled conditions the evolving reactions used in volatilization are quite specific, as with the action of hydrofluoric acid on silica. The residue often is left in good condition following a volatilization separation. In a number of cases a variety of methods is available for making the subsequent measurement of the desired constituent. Many substances require the use of only ordinary laboratory equipment. As to disadvantages in this method, special attention may be required to avoid "bumping" during evaporation, to control temperatures within certain limits, or to maintain satisfactory conditions for distillations. An additional possible disadvantage of volatilization is that most evaporations are slow.

CHAPTER 8

SEPARATION BY PRECIPITATION PROCESSES

The term "precipitation," as used here, refers to the formation of an insoluble substance in a solution of the sample. Considered more broadly, the process involves the separation of a solid phase from a liquid phase. This solid phase may be either an element, such as selenium or gold, or a compound, such as silver chloride or barium sulfate.

Occasionally, the term is applied to the separation of a solid or a liquid phase from a gas phase. In this sense, precipitation is often applied to the formation of rain. The Cottrell process of coagulating material dispersed in a gas is referred to as electrical precipitation.

In precipitation processes, as the term is used here, the desired constituent may be present in either the solid or liquid phase. Most frequently the solid phase formed contains the desired constituent, as in the separation of sulfur as barium sulfate. However, in many instances interfering constituents are removed as precipitates, the desired constituent then remaining in solution, free of interference.

The general subject of precipitation has received more attention in analytical texts and reference works than any other method of separation, but the subject has been treated primarily as a part of gravimetric methods[1] of measurement, rather than as a method of separation by itself. As noted in Chapters 3 and 16, the term "gravimetric" refers only to measurement by mass.

[1] Many authors have limited gravimetric methods to those involving precipitation of the desired constituent in the form of an insoluble solid. The presentation in this book is based upon the belief that the process of separation by precipitation has no essential connection with any particular kind of method of measurement.

In the determination of calcium, for example, the precipitation as the oxalate is the same, except for a final detail in washing, whether one is going to make a direct gravimetric measurement by weighing a suitable compound of the calcium, or an indirect titrimetric or colorimetric measurement of the metal by means of the reaction of a permanganate solution with the precipitated oxalate ion. Furthermore, the volume of the precipitate, if small, might be measured by collection of the solid in a centrifuge tube.

NATURE OF PRECIPITATION PROCESSES

The process of precipitation can be applied to the separation of both inorganic and organic substances. However, in an introductory book, the discussion is best confined, for the sake of simplicity, to reactions between ions in aqueous solution. The principles developed can be applied, of course, almost equally well to precipitation reactions involving nonionic species.

In an aqueous solution of sodium chloride, for example, we assume that the dominant ionic species are sodium, Na^+, and chloride, Cl^-, ions; similarly, in an aqueous solution of silver nitrate, the species are silver, Ag^+, and nitrate, NO_3^-, ions.[2] Addition of a few drops of a solution of silver nitrate to even a very dilute solution of sodium chloride results in the almost immediate formation of a precipitate of silver chloride, as every chemist knows. The process is interpreted in terms of the equation[3]

$$Cl^- + Ag^+ \rightleftarrows AgCl\downarrow \qquad (8.1)$$

An attempt to understand and interpret the many phenomena associated with such reactions would involve a more comprehensive survey of the chemistry of aqueous solutions than can be undertaken in this book. Attention is confined, therefore, to those aspects of the problem which seem of most direct interest to the analyst.

Stages in Precipitation

According to von Weimarn,[4] we may distinguish at least the following stages in a precipitation process taking place in a solution of electrolytes: (1) the collision of ions to form associated ions; (2) the aggregation of these associates to form a disperse colloidal system; (3) the further aggregation of colloidal particles to form visible particles; (4) the precipitation of the colloidally dispersed particles by the residual ions in solution; and (5) further changes, in the course of which the particles become larger to form a filterable precipitate and, in some cases, undergo a transformation to a more stable and less impure modification.

In making use of the process of precipitation our problem is to understand, as fully as possible, the nature of the phenomena associated with bringing a precipitate through these five stages and handling it after it is formed. Among the questions which may arise concerning the precipi-

[2] Hydration (solvation) of ions is disregarded here, in order to keep the treatment simple.

[3] Waldbauer (in *Theoretical Quantitative Analysis,* Blakiston, 1940) prefers to write the formula for silver chloride in the form Ag^+, Cl^-, in order to indicate that the precipitate is a solid composed of an orderly arrangement of silver, Ag^+, and chloride, Cl^-, ions.

[4] *Die Allgemeinheit des Kolloidenzustandes; Kolloides und kristalloides Lösen und Niederschlagen,* Steinkopff, 1925.

tation process, at least the following are important: (1) Will a reaction take place when two or more systems are brought together or when a system is subjected to some outside source of energy, such as heat, ultraviolet radiant energy, or electric current? (2) When does the reaction begin? (3) What products result from a given reaction? (4) How rapidly will the reaction proceed? What are the governing factors? How can the speed be controlled? (5) When does a precipitate first form? (6) Will the reaction go to completion? What will happen under specified conditions?

Many factors are involved in the manner in which a precipitation reaction is carried out, and in the use which can be made of the products of the reaction. Among the more pertinent facts that need to be known concerning the formation of a given precipitate are the following: (1) the conditions of reaction, including the temperature at which the reaction is best carried out, the concentrations of the reactants, the manner of mixing the solutions, and the agitation given to the medium of precipitation; (2) the speed of reaction, which has great effect on the nature of the precipitate obtained and which is in large degree controlled by the conditions of the reaction; and (3) the products formed, including the weight relationships, whether stoichiometric or empirical, between the reactants and products, and the purity of the products.

Reactions in Precipitation

Returning to the stages of precipitation postulated by von Weimarn,[5] it is evident that the analyst is concerned with the following sequence of reactions: ions → associated ions → colloidal aggregates → visible particles → filterable particles. The first of these transformations from ions to associated ions is one with which, to date, the analyst has had little concern except for the recognition that it is one step in the process.

The rate of transformation of ions to associated ions or molecules, and that of the reverse process, are assumed to be rapid. The state of the equilibrium between the ions and the molecules involved is defined by the dissociation constant, a topic that is considered later in this chapter. If a reaction does take place, it will accordingly proceed rapidly through the stage of associated ions, usually aided by an excess of common ions. If there is a reaction, it proceeds through this stage; the analyst is not concerned about stopping it at this point.

The subsequent transformations, which give rise to the formation of

[5] Various aspects of the process of precipitation are still under study. Christiansen, together with Nielsen, has reported results on (1) the time of formation of visible precipitates, (2) the formation of crystal "germs," and (3) the mechanism of precipitation of sparingly soluble salts. See *Acta Chem. Scand.* **5**, 673, 674, 676 (1951).

filterable particles, are of much concern. All filterable precipitates go through these stages in the course of their formation. Some reactions tend to produce particles that do not reach the filterable size readily. In some cases, the aim is to stop with colloidal aggregates. Some filterable particles undergo a reverse transformation on improper treatment. Colloidal aggregates have both desirable and undesirable properties. These and other points will now be considered.

COLLOIDAL PHENOMENA

A colloidal system consists of one substance, of suitable particle size, dispersed in another in which it is relatively insoluble. The former is called the *dispersed phase,* and the latter the *dispersing medium.* It must be emphasized that the terms "dispersed phase" and "dispersing medium" are only relative when applied to many types of dispersions. In case of doubt, the analyst considers the substance present in larger amount the dispersing medium.

A striking example of one kind of colloidal system is colloidal gold, which consists of metallic gold so finely divided that it remains suspended in water for years. This phenomenon calls for some interpretation when one considers that the density of gold is 19.3 and that of water is close to 1. The water is the dispersing medium and the gold the dispersed phase. Sometimes the water is referred to as the continuous phase and the gold as the discontinuous phase.

From substances in the three physical states, solid, liquid, and gaseous, nine combinations are possible: a *gas* in a gas, a liquid, or a solid; a *liquid* in a gas, a liquid, or a solid; and a *solid* in a gas, a liquid, or a solid. Of these possibilities, a gas in a gas is the only one which does not form a

TABLE 8.1

EXAMPLES OF COLLOIDAL SYSTEMS

Dispersed Phase	*Dispersion Medium*	*Examples*
Gas	Gas	(none)
Gas	Liquid	Foams, froth, suds, whipped cream
Gas	Solid	Meerschaum, pumice, blue jay feathers
Liquid	Gas	Fog, clouds, aerosols in general
Liquid	Liquid	Emulsions, homogenized milk, mayonnaise
Liquid	Solid	Gels; certain mercury ointments
Solid	Gas	Smoke, volcanic dust
Solid	Liquid	Sols; chocolate, paints
Solid	Solid	Ruby glass, black diamonds

colloidal system. In various applications of chemistry, the eight possible types are very important.[6] Examples of such dispersions are listed in Table 8.1.

The two colloidal systems of chief interest to the analyst are the dispersion of a liquid in a solid and the dispersion of a solid in a liquid. The former is known as a *gel* and the latter as a *sol.*

Properties

The colloidal state of matter is distinguished by the *size* of the particles dispersed. The criterion for the existence of a colloidal system has been the Tyndall effect.[7]

For some decades chemists have used the principles listed in Table 8.2 as one possible classification of disperse systems. Some of the characteristic properties of these systems are listed.

TABLE 8.2

PROPERTIES OF DISPERSE SYSTEMS

True Solutions	*Colloids*	*Suspensions*
Diam. <1.0 mμ*	Diam. 1.0 mμ to 0.1 μ	Diam. >0.1 μ
Not filterable	Not filterable	Filterable
Nonmicroscopic	Ultramicroscopic	Microscopic
Diffuse through membranes	Do not diffuse through membranes	Do not diffuse through membranes
	Increase in size of particles $\longrightarrow$	

* One micron, μ, is one-thousandth of a millimeter, and one millicron, mμ, is one-thousandth of a micron, or 10 A.

Substances having a particle size toward the lower limit of the colloidal range have, for a given mass, a tremendous surface area. Thus a cube 1 cm on the edge would have an area of 6 sq. cm. If this cube were subdivided into smaller and smaller cubes until the edge of each was 1 mμ,

[6] Colloidal systems are important in many areas other than chemical analysis, primarily because large numbers of the objects about us are colloidal in nature. Not only many of the articles of commerce and industry, but also protoplasm itself, the building block of all living matter, is essentially a colloidal system. One biologist characterized life as a series of satisfactions and dissatisfactions in a polyphasic colloidal system.

[7] In the Tyndall test a beam of light is passed through the system. If the system is colloidal in nature, light particles seem to be moving about in the cone of light. A familiar example is the apparent dance of dust particles in a beam of sunlight coming into a darkened room. The Tyndall effect is attributed to the reflection of light from the colloidal particles that are in constant motion as a result of Brownian movement.

the lower limit of colloidal dimensions, there would then be 10^{21} cubes, with a total surface of 6000 sq. meters. In comparison, one acre is 4047 sq. meters. An important effect of this great surface area is mentioned later.

Preparation

The two general methods available for preparing such dispersions may be predicted from an inspection of Table 8.2. Since the colloidal range lies between true solutions and suspensions, one should be able to reach the intermediate region from either direction. These processes are, then, (1) *condensation,* or the gathering together of small particles to form larger ones, and (2) *dispersion,* or peptization, the breaking up of large particles to form smaller ones. Practically, analysts often achieve just this latter result, although generally it is neither intentional nor desired.

The less common and, to the analyst, the less important method will be considered first. It consists in making particles of colloidal size from matter much less finely divided. Arcing electrodes of the noble metals under water is the classical example of a disintegration process. The term "dispersion" is usually applied to such a method. In analytical work one encounters this method only when von Weimarn's last stage of precipitation is reversed. This may happen when the precipitate is being washed after filtration.

Since a precipitation is made in order to remove some constituent, such a dispersive action is always undesirable. The common practice in trying to avoid it is to select a washing medium with no dispersive action. Thus, a precipitate of magnesium ammonium phosphate must be washed with a dilute solution of ammonium hydroxide rather than with water alone. Cold water will disperse a precipitate of silver chloride. There are many other examples of such peptizing action. During peptization by water, undoubtedly some particles go into true solution.

In the second method of preparation, the precipitation method, the dispersion is obtained by approaching the colloidal range from the opposite direction. Starting with true solutions, the particles of the dispersion are formed by a process of condensation or coagulation. Two common dispersions are of interest as examples. Colloidal hydrous ferric oxide, $Fe_2O_3 \cdot xH_2O$, may be prepared easily by pouring a solution of ferric chloride slowly into boiling water. A colloidal dispersion of silver chloride, which is not retained by the filter, may be obtained by mixing quickly very dilute, cold solutions of silver nitrate and hydrochloric acid. In the latter case it is important to note that the conditions of

formation specified are just the opposite of those usually recommended (Exercise 28.3) for obtaining an easily filterable precipitate of silver chloride.

As already stated, all filterable precipitates, in the course of their formation, pass through the range of colloidal dimensions. Generally, the analyst's chief concern with colloidal dispersions is to avoid them. However, there are occasions when his aim is to produce a dispersion sufficiently reproducible and stable for an analytical observation. Several examples illustrate such utility. Confirmatory tests for gold and platinum depend upon the production of dispersions of these metals having characteristic hues. The turbidimetric measurement of sulfur is based upon an optical method of comparison of two dispersions of barium sulfate. In the titrimetric method for silver involving the use of adsorption indicators (Exercise 27.4), the precipitate of silver chloride must be kept in the colloidal state for the method to work, i.e., the precipitate must not be allowed to coagulate and thus to grow in particle size.

An interesting relationship has been shown to exist between the concentration of the solutions used in a given precipitation and the average size of the particles produced when the reactants are brought together. The reaction between ferric chloride and potassium ferrocyanide is a good example. *Very* dilute solutions (about 0.0001 *M*) give a clear blue dispersion which passes at once through a quantitative filter paper. Solutions having a concentration of 5 per cent give a precipitate of good particle size, which is readily washable with water. The precipitate that is obtained when saturated solutions are poured together quickly is so finely divided that portions may be shaken up with water to form a blue dispersion similar to the one made with very dilute solutions. The optimum concentration for any particular precipitate usually must be determined experimentally or by analogy to past experiments. The usual concentration range for precipitants is approximately 3 to 5 per cent.

To conclude this brief statement regarding methods the analyst may pursue (intentionally or not) to produce colloidal dispersions, we may say that the product he obtains is, in large part, dependent on his understanding and controlling the factors operative for the particular system under observation. Thus, if a solution of ferric chloride is poured into water, the solution will be either simply diluted or hydrolyzed to the hydrous oxide, depending upon whether the water is, respectively, cool or boiling. The analyst's practice must be guided, to a large extent at least, by accumulation of the results of much empirical study of different systems under a variety of conditions.

Analytical Use of Colloidal Properties

From the standpoint of the analytical significance of colloidal dispersions, various properties of such systems are of importance in quantitative separations and measurements. The more important of these characteristics—hue, size of particles, stability—including the analytical use made of each and the nature of the problem that it presents, will be discussed briefly.

A striking property of certain sols is their *hue*. The confirmatory tests for gold and platinum, already mentioned, are based upon this effect. The hue of gold sols varies from red to blue, the difference depending upon the size of the dispersed gold particles.

Particle size is the distinguishing characteristic, of course, of all colloidal dispersions. This property is of concern to the analyst in several ways. In precipitation separations the aim is to produce a precipitate the particles of which are large enough to be retained by the filtering medium used. The retention must be satisfactory not only during the filtering of the mother liquor but also during completion of the washing. Any failure to secure adequate coagulation of the sol in the course of the formation of the precipitate, or any peptization of the precipitate during washing will result in the loss of colloidally dispersed particles through the filter. Consequently, there will be a deficiency in the amount of the precipitate obtained, and a resultant error in the determination.

The size of the particles is also very important in a colloidal dispersion upon which a turbidimetric measurement[8] is to be based. The dispersion must be reasonably reproducible and sufficiently stable to permit the measurement to be made. Otherwise, reliance could not be placed on the optical scattering of the light beam in the turbidimeter.

A third way in which size of the particles is important in analysis has to do with the carrying down by the precipitate of substances soluble in the solution. This action is often called "adsorption." Its effects are discussed later in connection with the subject of the purity of the precipitate. The aim here is to point out that, insofar as the adsorptive process may be attributed to the attraction of surface forces for the substances adsorbed, the extent of adsorption will be proportional to the surface exposed. Other factors being equal, very finely divided precipitates, and those which are coarse but pass very slowly through the colloidal range, may be expected to show the most contamination.

[8] A turbidimetric measurement is one in which the amount of light reflected from a suspension is compared to that reflected by standard suspensions in order to estimate the amount of material in the unknown suspension. It is thus a quantitative method based on the Tyndall effect previously described (see also Chapter 19).

In order to minimize this impurity, and to obtain particles of suitable size, the analyst generally observes certain precautions in producing precipitates that are to be filtered. The conditions represent, substantially, a reversal of those recommended in the illustration of the precipitation method for making a colloidal dispersion. The solution from which the precipitate is to be separated is usually heated nearly to boiling, the precipitant is added slowly, and the system is stirred during precipitation. This procedure generally aids in the formation of large-sized particles.

Some reference has already been made to the *stability* of colloidal dispersions. Occasionally the analyst wants to keep the system in the colloidal state, at least for a short time. To do so means that the successive stages of coagulation postulated by von Weimarn must be interrupted or their speed greatly retarded. Some systems, prepared under suitable conditions, are relatively stable; hardly any precautions, for example, are required to prepare a stable sol of hydrous ferric oxide. However, most systems coagulate, to some extent, in a short time. When one wishes to enhance the stability of certain systems, the dispersion may be formed in the presence of a protective material or stabilizer (e.g., gelatin functions in this way for certain materials). In the Fajans' method for determining chloride ion, advantage is taken of the action of a surface-active substance in retarding the coagulation of silver chloride (Exercise 27.4).

The mechanism of the process of coagulation of sols has been studied extensively. Nearly all such dispersions are electrically charged, as a result of the adsorption of ions. In general, electrolytes tend to bring about flocculation of colloidal particles but there is much variation in the effectiveness of such coagulants. Some cause little change. Ferric chloride hydrolyzed by pouring a solution into boiling water needs no stabilizer, nor does it have to be dialyzed[9] to remove any electrolyte which might coagulate the dispersion. In this case the colloidal particle is believed to be highly hydrated, and this seems to increase the stability. However, the addition of two to three drops of concentrated sulfuric acid to such a system causes an immediate precipitation of the hydrous ferric oxide. Colloidal gold is relatively instable unless dialyzed. As a rule, the effectiveness of coagulation is directly proportional to the number of charges on the coagulating ion. This coagulating action of an electro-

[9] In the process of dialysis the colloidal suspension is confined in a cellophane or similar semipermeable membrane sack and placed in water. The ions of the electrolyte diffuse through the membrane until the concentrations of the ions are approximately equal in both the sack and the water solution. The colloidal particles are too large to diffuse through the membrane. By the successive replacement of the water, it is possible to decrease the electrolyte content of the colloidal suspension to a very low value. The purpose of dialysis is to prevent the coagulation of the colloidal suspension by the electrolyte.

lyte presumably accounts for the fact that silver chloride or lead molybdate will be dispersed on washing with water, but will not be so affected if one uses, respectively, a solution of nitric acid or ammonium nitrate.

The mutual repulsion of the electrically charged colloidal particles contributes to the stability of the dispersed system. Also these charged particles tend to adsorb ions of the opposite charge. It is this adsorptive process involving electrical charges which is the basis for the end point indication in Fajans' method previously mentioned.

It is frequently stated that coagulation is aided by boiling, stirring, or shaking the system. Many precipitates do seem to form filterable aggregates more readily with these treatments, which, in all probability, effect an acceleration of the coagulation process already underway. Nearly all students of qualitative analysis have recollections of difficulty in finding any means of coagulating sols of arsenic or antimony sulfide.

EQUILIBRIA IN MIXTURES OF PRECIPITATE AND SOLUTION

The analyst is concerned with the equilibria involved in the over-all transformation of ions into insoluble particles of a precipitate.

As has already been stated, two solutions, forming an insoluble substance on reacting with each other, may exhibit no visible evidence of formation of the expected precipitate. The fact that the substance is invisible is usually attributable to the formation either of a clear colloidal dispersion, or of a supersaturated solution. A third possibility is that not enough product to saturate the solvent may have been formed. Every solid has a definite solubility in a given solvent under specified conditions. A saturated solution may be made by stirring the solid with an amount of solvent insufficient to dissolve all the material. At a given temperature a state of equilibrium is attained where there is no further change in the concentration of the solution in contact with the solvent. For a saturated solution of a substance, such as silver chloride, we may consider that, at equilibrium, there are two opposing reactions:

$$\text{Solid solute} \rightleftarrows \text{dissolved solute}$$

Applying the equilibrium expression, at any given temperature we have

$$\frac{[\text{AgCl}]_{\text{dissolved}}}{[\text{AgCl}]_{\text{solid}}} = K_1$$

Since the thermodynamic activity of a solid is a constant for a given temperature, $[\text{AgCl}]_{\text{solid}}$ is a constant. Consequently,

$$[\text{AgCl}]_{\text{dissolved}} \rightleftarrows [\text{AgCl}]_{\text{solid}} \times K_1 = K_s \tag{8.2}$$

where K_s is the solubility constant.

At any given temperature, therefore, a definite concentration may be expected for a saturated solution, that is, a solid has a definite solubility. The fact that solubility is also dependent upon the particle size of the solid substance in contact with the solution does not appreciably affect the ordinary solubility. This phenomenon is of practical importance only during the early stages of formation of a precipitate.

When the solid is being formed in the solution, precipitation should occur as soon as the value of K_s is exceeded, unless a state of supersaturation or a colloidal dispersion intervenes. In an ideal system this relation would apply whenever the solution is saturated with the solid, regardless of the presence of other substances or of any decomposition products of the substance itself.

Solubility Product Principle

If the solid postulated in the preceding section is an electrolyte, such as silver chloride, another aspect to the equilibrium represented by a saturated solution must be considered. When the silver chloride is in equilibrium with its ions and with water, the system may then be represented by the expression

$$[\mathrm{AgCl}]_{\mathrm{solid}} \rightleftarrows \mathrm{Ag^+} + \mathrm{Cl^-} \tag{8.3}$$

Then

$$\frac{[\mathrm{Ag^+}] \times [\mathrm{Cl^-}]}{[\mathrm{AgCl}]} = K \tag{8.4}$$

And as the concentration of the solid silver chloride may be taken as a constant, we have

$$[\mathrm{Ag^+}] \times [\mathrm{Cl^-}] = K_{\mathrm{sp}} \tag{8.5}$$

K_{sp} is the solubility, or ion, product constant. For a saturated solution of a slightly soluble, ionizable solid, this expression shows that (1) the product of the concentrations of the ions has a definite value, characteristic of the solute at a given temperature; (2) there will be no precipitation of a given compound until the product of the concentration of its ions exceeds the ion product; and (3) the compound will dissolve in the solvent until the product of the concentration of the ions reaches the value of the ion product constant.

In order to calculate the solubility product constant of a given compound, we must know the concentration of the ions in moles per liter. This value is calculated from the molar solubility of the substance and the effective ionization of the compound. The latter value is taken as 100 per cent for slightly soluble compounds, such as silver chloride and

barium sulfate. This method of calculation is illustrated for lead chromate and lead chloride.

The solubility of lead chromate is 0.0001 g per liter at 18°, and the molecular weight is 323.2. The molarity of a saturated solution is $0.0001/323.2 = 0.0000003\ M = 3 \times 10^{-7}\ M$. As the effective ionization is assumed to be 100 per cent, and since 1 mole of lead chromate gives 1 mole each of lead (Pb^{++}) and chromate (CrO_4^{--}) ions, the concentration of each ion is $3 \times 10^{-7}\ M$. Therefore,

$$[Pb^{+2}] \times [CrO_4^{-2}] = (3 \times 10^{-7})^2 = 9 \times 10^{-14} = K_{sp} \text{ of } PbCrO_4$$

Compared to the calculation for lead chromate, that for lead chloride has three points of contrast: the solubility is much larger, the effective ionization is lower, and there are two chloride ions for each lead ion. The solubility at 20° is 9.75 g per liter, and the molecular weight is 278.1. A saturated solution is $9.75/278.1 = 0.035\ M$. The effective ionization may be taken as 70 per cent. Since 1 mole of lead chloride gives 1 mole of lead ion (Pb^{++}) and 2 moles of chloride ion (Cl^-) the concentration of lead ion is $0.0245\ M$ (70 per cent of 0.035) and that of chloride ion is $0.049\ M$ (70 per cent of 2×0.035). Then

$$[Pb^{+2}] \times [Cl^-]^2 = 0.0245 \times 0.049^2 = 0.00006 = 6 \times 10^{-5}\ M = K_{sp} \text{ of } PbCl_2$$

It should be noted that the concentration of the chloride ions is squared.

Common-Ion Effect

In the discussion of solubility and of the ion product principle it has been assumed that the system under consideration consisted only of some individual compound in contact with the solvent. The next point of interest is the effect produced by the presence of other soluble, ionizing substances. There are two possibilities: (1) the second solute contributes an ion that is common to the two solutes, as would be the case on addition of potassium chloride to a saturated solution of silver chloride; and (2) the second solute contributes only diverse ions, as would be the case on addition of potassium nitrate to a saturated solution of silver chloride. The effects will be considered separately.

The presence of a second solute which forms an ion in common with the first solute gives rise to what is known as the "common-ion effect." This term refers usually to the lowering of solubility of a compound caused by the presence of a substance having one ion in common with those of the sparingly soluble compound. A knowledge of the implications provides a basis for answering, partially at least, questions such as the following: (1) Will silver chloride dissolve to the same extent in water alone as in

a solution 0.01 M sodium chloride? (2) What will be the effect of adding different amounts of a precipitant in excess? (3) Is complete precipitation theoretically possible? (4) At what ratio of reactants is the solubility of the precipitate a maximum?

Let us now return to equations (8.4) and (8.5). We have already stated that the product of the concentration of the ions is a constant. Therefore, if one increases the concentration of one of the ions, the concentration of the other must decrease in order to maintain constancy of the ion product. The addition of sodium chloride or of hydrochloric acid, for example, to a saturated solution of silver chloride should thus reduce the concentration of the silver ion. From the equations it is obvious that this result can be achieved only by shifting the equilibrium toward the left through the formation of more solid silver chloride, that is, the solubility of the silver chloride is decreased. A similar result would accompany an increase in the concentration of the silver ion.

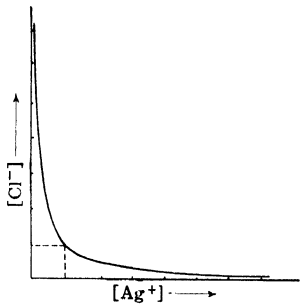


Figure 8.1
Cl^-/Ag^+ ratio.

Consideration of this common-ion effect leads to the conclusion that the solubility of silver chloride, for example, is at a maximum when the concentrations of the silver and the chloride ions are equal. The general relationship is illustrated in Figure 8.1. The curve, representing the solubility of silver chloride at different concentrations of the ions, is an equilateral hyperbola for univalent salts.

Numerical calculation shows that a slight excess of precipitant reduces the solubility very markedly. Thus, the solubility product of silver chloride is 1.9×10^{-10} at 30°. The concentration of each ion in a saturated solution would then be

$$\sqrt{1.9 \times 10^{-10}} = 1.38 \times 10^{-5}\ M.$$

If the concentration of the silver ion is increased to 0.001 M, the concentration of the chloride ion $= 1.9 \times 10^{-10}/0.001 = 1.9 \times 10^{-7}\ M$. This action accounts for the frequent directions in laboratory manuals and elsewhere to "add an excess of precipitant." It is evident, however, that theoretically complete precipitation is impossible, since one cannot reduce the concentration of either ion to zero. Nevertheless, the point of equilibrium can be changed and the reaction pushed more nearly to completion.

Effect of Large Excess of a Common Ion

Although a small excess of a precipitant has been shown to produce a favorable effect, in that it decreases the solubility of the precipitate, considerable excess may have quite the opposite effect. First of all, the general role played by interionic forces must not be neglected in judging the application of the solubility product principle. Difficulty arises if one assumes that the solubility product remains constant under all ionic concentrations. Lanthanum iodate may be taken as an example of a change in solubility product with change in ionic concentration. Assuming constancy of the ion product, lanthanum iodate should be less and less soluble in lanthanum nitrate solutions of increasing concentration. The data in Table 8.3 are significant. At first the solubility of the lanthanum iodate decreases because of the common-ion effect, then it increases in spite of this effect. The second effect, resulting in increased solubility, may be attributed to the general build-up of ionic concentration in the solution.

TABLE 8.3

SOLUBILITY OF $La(IO_3)_3$ IN SOLUTIONS OF $La(NO_3)_3$

$La(NO_3)_3$ *Added* (M)	$La(IO_3)_3$ *Solubility* (M)	$La(IO_3)_3$ K_{sp} (M)
0	9.48×10^{-4}	2.2×10^{-11}
16.7×10^{-4}	8.35×10^{-4}	3.9×10^{-11}
33.3×10^{-4}	8.10×10^{-4}	5.9×10^{-11}
166.7×10^{-4}	8.70×10^{-4}	3.3×10^{-10}
333.3×10^{-4}	9.40×10^{-4}	7.7×10^{-10}

The steady increase in the solubility product values, as shown in Table 8.3, is significant, too. By definition, the solubility product is a constant. The lack of constancy shown here may be attributed to the use of molar concentrations, rather than activities for the ions. The activities change with the total ionic concentration, since the activity coefficient decreases with increase in the ionic strength of the solution. According to Kilpatrick,[10] deviations from ion products calculated according to equation (8.5) may be largely eliminated by using the activities of the ions. Textbooks on general physical chemistry may be consulted for details of the activity concept and its application.

[10] *J. Chem. Educ.* **9**, 843 (1932).

Application of Common-Ion Effect

In considering the application of the principle of the common-ion effect, several points should be kept in mind. The principle is more nearly true (1) the smaller the solubility of the compound, (2) the simpler the valence type of the compound, and (3) the smaller the concentration of diverse ions, as indicated in the section to follow. The principle is most nearly true for extremely dilute solutions of salts with an ion in common with one of the precipitate. The effect of a slight excess (0.001 to 0.01 *M*) of the precipitant is generally in qualitative agreement with the principle, and is approximately in quantitative agreement. The agreement between theory and observation is best for uniunivalent electrolytes. A large excess of precipitant (1 *M*) is likely to increase the solubility of the precipitate, as illustrated by the data in Table 8.3.

In addition to increase in solubility of a precipitate, as a result of the action of a common ion, other possible causes of increase in solubility must be kept in mind. For instance, in the precipitation of hydrous aluminum oxide, the analyst is directed to add only a slight excess of the precipitant, ammonia. The solubility of the precipitate in excess precipitant is attributed by some to the amphoteric nature of aluminum hydroxide. In the presence of excess base, the equilibrium represented by the equation

$$H_2O + AlO_2^- + H^+ \rightleftarrows Al(OH)_3 \rightleftarrows Al^{+3} + 3\ OH^-$$

is shifted to the left, because of the decrease in hydrogen ion concentration.

Advantage is taken in brass analysis of a related action to facilitate a separation. A distinct excess of ammonium hydroxide is added for the separation of iron and zinc. The excess is necessary to dissolve any zinc hydroxide precipitated along with the iron. The slightly dissociated zinc-ammonia complex ion $Zn(NH_3)_4^{+2}$ thus formed decreases the concentration of the zinc ion to the point where the solubility product of zinc hydroxide is not exceeded. These simple cases are examples of the general use of excess reagent to form soluble compounds.

A less common kind of action is the dispersing of a precipitate by excess precipitant. Some analysts have maintained that the previously mentioned dissolution of aluminum hydroxide is attributable, at least in part, to peptization by the excess base, rather than to complex formation.

Diverse-Ion Effect

In the previous discussion consideration has been given to the effect on the solubility of a slightly soluble compound of an ion in common

with one of its ions. As indicated, many examples can be found where the common ion increases, rather than decreases, the solubility of the slightly soluble compound.

An increase in solubility is also found in the presence of many compounds contributing no ion in common with those of the slightly soluble substance. Such action may be called a "diverse-ion effect." To illustrate the phenomenon, Table 8.4 contains data on the solubility of thallous chloride in the presence of several different compounds.[11] The effects of the compounds contributing no common ions is evident.

TABLE 8.4

SOLUBILITY OF TlCl IN THE PRESENCE OF DIFFERENT COMPOUNDS
(The solubility of TlCl alone, for the conditions studied, is 16.12 milliequivalents per liter.)

COMPOUND CONTAINING COMMON ION			COMPOUND CONTAINING DIVERSE ION		
Formula	*Amount Added in Millieqs.*	*TlCl Dissolved, in Millieqs.*	*Formula*	*Amount Added, in Millieqs.*	*TlCl Dissolved, in Millieqs.*
HCl	25	8.69	$NaC_2H_3O_2$	15	16.8
	50	5.85		30	17.2
	100	3.84		79	18.5
	200	2.54		157	19.6
KCl	25	8.72	KNO_3	20	17.2
	50	5.92		50	18.3
	100	3.97		100	19.6
	200	2.69		300	23.1
$TlNO_3$	25	8.83	K_2SO_4	20	17.8
	50	6.26		50	19.4
	100	4.23		100	21.4
				300	26.0
Tl_2SO_4	20	10.34			
	50	6.77			
	100	4.68			
$CaCl_2$	25	9.01			
	50	6.20			
	100	4.17			
	200	2.83			

Such effects may be interpreted in terms of the interionic forces prevailing in the system. The electrostatic environment of the precipitate in the presence of such a combination of ionic species undoubtedly affects the solubility by altering the activities of the ions in equilibrium with the precipitate.

[11] Noyes, *J. Am. Chem. Soc.* **46**, 1107 (1924).

Regardless of the nature of the mechanism which operates to produce the diverse ion effect, the data in Table 8.4 show that its magnitude is sufficient, and so variable for different substances, that it cannot be neglected. In actual precipitation separations there is, generally, in the solution at least one compound furnishing diverse ions. As yet, calculation, in a given case, of the effect of several such ions in concentrated solutions, is difficult. Usually it is much simpler to determine experimentally what the effect is under a given set of conditions.

Other Technics for Decreasing Solubility

In addition to decreasing the solubility of a compound by the common-ion effect, the analyst may minimize solubility losses in other ways. One obvious method is to reduce the volume of solution in which the precipitation occurs. This technic is used in the precipitation of a triple acetate of sodium, e.g., sodium magnesium uranyl acetate.

A second technic involves a change in the solvent used. Thus, the addition of certain organic liquids to water will usually decrease the solubility of ionic compounds. For instance, calcium sulfate, which is appreciably soluble in water (0.2 g per 100 ml), can be almost completely precipitated in a solution which is 10 per cent water and 90 per cent methanol. The optimum ratio of organic solvent to water may be calculated.[12]

Lowering the temperature often results in a decrease in solubility. Thus, whereas barium sulfate is filtered from a hot solution to speed up the operation of filtration, the more soluble lead sulfate must be filtered from a cold solution.

Supersaturation

In the discussion of colloidal dispersions there was mention that when two solutions, the components of which interact to form an insoluble substance are brought together, a filterable, or even visible, precipitate might not be obtained. This result was attributed to the very finely divided state of the product of the reaction. Many sols, for example, appear entirely clear.

A similar, but apparently different, phenomenon is known as "supersaturation." Some substances can be dissolved to an extent far in excess of the amount that will remain in solution when the solution is in equilibrium with the solid solute. When the magnesium ion is precipitated as magnesium ammonium phosphate hexahydrate, small amounts of the metal ion often show no evidence of the formation of a precipitate (Exer-

[12] Robinson, *Anal. Chem.* **26,** 1156 (1954).

cise 31.2). In this particular case, the assumption that magnesium is absent is never safe until the solution has stood 10 to 12 hours. Even then, if the solution is still clear, the inside wall of the beaker should be rubbed with a stirring rod below the surface of the solution to induce separation of any precipitate.

The tendency of precipitates to form supersaturated solutions varies widely with different elements, or with different compounds of the same element. Observation of the properties of many precipitates has led to the general conclusion that supersaturation is probably involved to some extent in all precipitation processes.[13]

Supersaturation may be explained, at least in part, by the slowness with which the sequence of stages in precipitation, described earlier in this chapter, may occur. Although most ionic reactions are practically instantaneous, there are exceptions. The formation of a complex ion, such as molybdophosphate $[P(Mo_3O_{10})_4]^{-3}$ may be slow. Supersaturation may be a stage in slow precipitation because of slow passage through the colloidal stage. The kinetics of the precipitation of barium sulfate, i.e., the rate at which the precipitate forms, has been studied and an induction period observed.[14] Reactions involving nonionized substances, such as organic compounds, are also likely to be slow.

The time required for any reaction may be much reduced by agitation or vigorous stirring of the solution, by moderate excess of the precipitant, by an increase in the temperature at which precipitation is made, or by a combination of these effects.

Digestion

Most precipitates must stand in contact with the mother liquor for some time to complete the process of aggregation into filterable particles. "Digestion" is the term commonly applied to this process in which the particles of the precipitate are permitted to remain in contact with the solution for a period of time varying from minutes to hours, or, in rare cases, days.

Precipitates such as barium sulfate are usually digested at a temperature near the boiling point of the solution by placing the vessel containing the precipitate over a low flame or on a steam bath or hot plate. In contrast, the digestion of magnesium ammonium phosphate is accomplished by setting the vessel aside for 12 to 24 hours at room temperature, since a high temperature would produce an undesirable change in the composi-

[13] For a general discussion of the phenomenon of supersaturation, see Smith, *Analytical Processes*, Arnold, London, 1940.

[14] Duke, Beaver, and Diehl, *Iowa State Coll. J. Sci.* **23**, 297 (1949).

tion of the product (see "Analysis of Limestone: Magnesium," p. 574).

There has been much speculation as to the processes that probably occur during digestion, and the causes of the effectiveness of the digestive process. In general, the efficiency of digestion is attributable in large part to the processes of Ostwald ripening and Kolthoff aging.

The basis for the ripening theory, which was proposed many years ago by Ostwald, is the difference in solubility of small and large particles. It has been shown, both theoretically and experimentally, that the solubility of substances increases as their particle size decreases. Consequently, when a solvent is in contact with a mixture of both small and large particles of the same precipitate, it will be saturated with respect to the large particles before it is saturated with respect to the small particles. As a result, the small particles dissolve. Since the solution then becomes supersaturated with respect to the large particles, the excess of the solute deposits out on the large particles. The small particles therefore disappear as the large particles become still larger.

For some years Kolthoff and some of his students have studied the nature of entrainment and the purity of precipitates (see the section following). From their work it is evident that the process of digestion involves factors in addition to ripening of the Ostwald type. In particular, a process of self-perfection of crystals occurs. Kolthoff has used the term "aging" for the transformation that occurs in the precipitate during digestion. The following quotation is from an early article summarizing conclusions he had then reached.

> In extensive studies on the aging of freshly precipitated lead sulfate prepared from 0.1 molar lead nitrate and 0.1 molar potassium sulfate at room temperature we arrived at the conclusion that the classical type of aging, the so-called Ostwald ripening, is of subordinate significance at room temperature. When dealing with a heterodisperse precipitate the Ostwald ripening involves the solution of the smaller particles and the growth of the larger particles at the expense of the small ones. Recent studies on the aging at room temperature of barium sulfate and of silver chloride have substantiated the above conclusion. The fresh precipitates, although crystalline, are highly imperfect, as indicated by the diffuseness of the X-ray lines. Especially during the early stages of aging in the mother liquor a very fast perfection process occurs as a result of recrystallization without *always* being accompanied by pronounced changes of the external surface (Ostwald ripening).
>
> It was found that all factors which decrease the solubility of the precipitate inhibit the speed of perfection, and hence of recrystallization; on the other hand, all factors which increase the solubility promote recrystallization and perfection. It was concluded that this recrystallization occurs in a liquid film around the primary particles. The surface of the latter is very irregular and contains spots

of various activities. At these spots ions quickly enter into the liquid film, the solution being supersaturated with regard to the more normal surface, on which the ions redeposit. This process occurs so quickly that the lattice ions, in excess in the supersaturated film, hardly have an opportunity to enter the bulk of the solution and cause Ostwald ripening. The recrystallization, therefore, results in a self-digestion and self-perfection of the primary particles.

The speed of perfection is not determined by the solubility of the precipitate in the bulk of the solution but by the solubility in the liquid film around the particle. Thus, barium sulfate ages much faster in 0.005 M. sulfate than in 0.005 M. barium solution, although the solubility of the precipitate in both solutions is of the same order. The difference is attributed to the fact that barium ions are adsorbed much stronger on the fresh precipitate than sulfate ions. Consequently, the solubility of the barium sulfate in the liquid film around the particles is much smaller in 0.005 M. barium than in 0.005 M. sulfate.

In studies with freshly precipitated silver chloride it was found that the aging is much more pronounced in 0.001 M. chloride than in 0.001 M. silver. In interpreting this result it should be realized that the silver halides have a pronounced tendency to adsorb their own ions, the halide ions being more strongly adsorbed than silver ions. Thus, the concentration of the adsorbed chloride ions in the solvated jacket around the particle may be much greater than in the bulk of the solution and may give rise to the formation of the complex $AgCl_2^-$ ions with the silver chloride. It is well known that the solubility of silver chloride in more concentrated chloride solutions is greater than in water, owing to formation of complex argento-chloride ions. If the concentration of the adsorbed chloride ions in the liquid film is great enough, the solubility of the silver chloride in the liquid jacket may be much greater than in the bulk of the solution, thus accounting for the more rapid aging of silver chloride in 0.001 M. chloride than in 0.001 M. silver or in pure water.

So far, we have only considered the perfection of the individual particles. This process may be accompanied by an agglomeration. Various primary particles may share their water jackets and thus form loose agglomerates which can be easily peptized again. When the perfection process occurs in such an agglomerate, lattice ions may be deposited in the liquid canals between the particles, thus cementing them together by the formation of bridges consisting of lattice material. When the entire liquid space is filled up with lattice material, the crystalline aggregates will have a mosaic structure. The cementing process is irreversible and results in a decrease of the total surface of the precipitate as measured by the adsorption of a suitable dye. Factors which promote the perfection process will also promote the cementing process. It was found, for example, that no cementing occurred upon the slow aging of barium sulfate in a solution containing an excess of barium but a very pronounced one upon the aging in excess of sulfate. Also, the aging of silver chloride in an excess of chloride and even of silver is accompanied by a pronounced cementing process.[15]

[15] Kolthoff, *Science* **84**, 376 (1936). For experimental details, see a long series of articles by Kolthoff and students, chiefly in *J. Am. Chem. Soc.*

Types of Precipitates

The precipitates in quantitative work show much variation in physical characteristics. A number of more or less distinct types are recognized. Magnesium ammonium phosphate hexahydrate is crystalline, lead sulfate is pulverulent, silver chloride is curdy or flocculent, and hydrous ferric oxide is gelatinous or amorphous. Presumably the differences in physical types may be attributed largely to differences in internal structure. The apparent physical state of a precipitate is often influenced by the conditions under which precipitation is made.

ENTRAINMENT AND PURITY OF PRECIPITATES

Thus far it has been assumed that a precipitate consists only of the pure substance which should separate for the reaction involved. Such an assumption implies reliance upon the validity of the law of constancy of composition of compounds. Also, each time a calculation is based upon the weight of an unexamined residue in a gravimetric determination, the purity of the substance is assumed to be 100 per cent.

Although to have precipitates that yield, on drying or ignition, residues that are uncontaminated and of definite composition would be highly desirable, an examination of the chemical literature leads to the conclusion that the purity of every precipitate must be questioned. Some compounds, such as silver chloride, usually do separate in practically pure form; but many, such as barium sulfate, generally do not. In fact, contamination is so general and, often, of such magnitude, that the subject deserves special consideration.

The term "entrainment" is used in a general sense to refer to the retention by a precipitate of soluble constituents of the solution from which it separates in such a way that continued washing will not remove them. The British term "sorption" may be used in the same sense. Other terms, such as "occlusion," "adsorption," "coprecipitation," and "post-precipitation," have been used in a general sense but their originators intended, rather, to refer to what were believed to be different kinds of contamination.

All precipitates entrain foreign substances to a greater or lesser extent. The phenomenon is important not only in analytical chemistry, but also in the use of fractional crystallization to separate pure compounds, in the preparation of catalysts, and in geochemical studies. Entrainment is also used in the isolation of very minute amounts of materials by preferential adsorption, as in the separation of elements produced by nuclear bombardment. It is also used in the determination of surface area of solids, and in the purification of drugs and various other substances.

The factors involved in entrainment have been studied by the use of radioactive tracers, X-ray diffraction patterns, emission spectroscopy, electron microscopy, and other technics for examining precipitates under carefully controlled conditions. Such studies of the variables affecting the extent of entrainment have revealed the conditions under which precipitation can be performed with a minimum of contamination. Theoretical considerations show the following factors, in addition to solubility, to be important in determining the extent of entrainment: (1) the type of crystal lattice of the precipitate; (2) the nature and properties of the compounds formed by the ions of the precipitate with the foreign ions present in the solution; and (3) the size, charge, configuration, and polarizability of the ions involved.

Types of Entrainment

Generally the analyst's primary concern with entrainment is to avoid it, or to correct for it. A secondary concern is to understand something of the ways in which a precipitate becomes contaminated. This knowledge enables him to avoid, or at least to minimize, errors resulting from entrainment.

We are concerned here with the contamination of solids by gases, liquids, and other solids. The contamination of precipitates by gases is usually negligible. However, contamination of ignition residues by gases produced during decomposition of the precipitate is possible, if these gases are not removable except at temperatures at which the residue decomposes.

Contamination of a solid precipitate by liquids is somewhat more common. Mechanical adhesion of the mother liquor, i.e., the solution in which precipitation occurred, is usually easily corrected by thorough washing of the precipitate. Mechanical inclusion of mother liquor by the forming precipitate is a possibility; this effect is less probable with well-crystallized precipitates than with those of gelatinous nature, such as hydrous aluminum and stannic oxides. Fusion of the precipitate, if feasible, may not always remove the difficulty, since a residuum of salts may be left on escape of the solvent from the fused residue.

The most difficult, as well as the most common, case of entrainment is that of the desired solid precipitate contaminated by other solids at the temperatures involved. The types of entrainment involved may be considered to be coprecipitation and postprecipitation.

Coprecipitation refers to any of the kinds of contamination that occur during the course of the formation of the precipitate. *Postprecipitation* usually designates entrainment that occurs after the precipitate has been

formed. A frequently cited example of the latter type of entrainment is the separation of calcium from magnesium by precipitation of the calcium as the oxalate. All of the calcium precipitates, but it carries some impurities. If the precipitate stands for long before filtration, it becomes increasingly contaminated with magnesium oxalate; the latter substance is said to be postprecipitated. The possibility of such postprecipitation provides a good reason for not delaying filtration of a precipitate any longer than necessary.

The *causes* of entrainment are not only mechanical, as in physical inclusion, but also chemical, i.e., bonding of various kinds between the desired constituent and the contaminants. There may be indefinite composition of the precipitate, compound formation, solid solution formation, mixed crystal formation, and adsorption.

Improper composition of a part, or the whole, of the precipitate usually results from improper composition, concentration, or temperature of the solution in which precipitation occurs. For example, magnesium is often precipitated as magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6\,H_2O$, which on ignition is converted to the pyrophosphate, $Mg_2P_2O_7$, for weighing. Improper concentration of ammonia and ammonium salts may result in the precipitation of more or less magnesium as the diammonium phosphate, $Mg[(NH_4)_2PO_4]_2$, which, on ignition, is converted to a metaphosphate, $Mg(PO_3)_2$. Erroneous values then result, if the calculations assume the residue to be the pyrophosphate, $Mg_2P_2O_7$.

In a few instances a definite compound forms between the precipitate and a substance in the solution. Examples of such insoluble, double salts are potassium-lead sulfate, $K_2SO_4 \cdot PbSO_4$, and potassium-lanthanum oxalate, $KLa(C_2O_4)_2$. This type includes complex, slightly soluble basic salts. Actually, formation of such definite chemical compounds is rare under the usual conditions of analytical precipitation. Another type of entrainment is the formation of mixed crystals as a solid solution or isomorphous mixture. This result may arise when the contaminating constituent has ions of approximately the same dimensions and lattice properties as those of the precipitate. The impurity takes its place in the crystal lattice of the insoluble compound, and presumably remains distributed in the interior of the solid particles. A careful X-ray study of the contamination of barium sulfate by the nitrate ion[16] indicated that the process is solid solution. Other possibilities have been suggested.[17] Many studies have been made in an effort to distinguish between two other kinds of entrainment for which the terms "occlusion" and "adsorp-

[16] Walden and Cohen, *J. Am. Chem. Soc.* **57**, 2591 (1935).
[17] Schneider and Rieman, *J. Am. Chem. Soc.* **59**, 354 (1937).

tion" have been rather generally used, sometimes synonymously. Ostwald thought of adsorption as the result of an attractive or restraining physical force exerted by the solid to hold the dissolved substance in the immediate neighborhood of the bounding surfaces, and serving either to retard, or entirely prevent, the removal of these substances by washing. Richards used the term "occlusion" and thought of the process as being chemical rather than physical. Kolthoff applies the term "occlusion" to entrainment taking place during the growth of the crystal where the impurity is not in the lattice but rather forms imperfections in the crystal. The term "inner adsorption" has been used also for this kind of action. "Surface adsorption" then refers to entrainment taking place after the precipitate forms.

Extent of Entrainment and Factors Involved

Certain other items concerning the extent of entrainment and some of the factors involved may be mentioned. The phenomenon is of rather general occurrence, all precipitates showing more or less tendency to entrain soluble constituents. The degree of entrainment differs widely. Some precipitates are virtually free of entrainment, although doubt has been expressed that any compound conforms absolutely to the laws of definite and multiple proportions.[18] On the other hand, certain soluble substances are so completely adsorbed that the process is made the basis of quantitative separations (see Chapter 10).

TABLE 8.5

POSITIVE ERROR PRODUCED BY PRECIPITATION OF BARIUM SULFATE IN THE PRESENCE OF POTASSIUM NITRATE

KNO_3 added, g	0.0000	0.2000	1.0000	5.0000
Weight of $BaSO_4$, g	1.0133	1.0180	1.0300	1.0472
Excess weight, g*	0.0015	0.0062	0.0182	0.0354
Error, per cent	0.14	0.61	1.79	3.49

* Calculated for 1.0118 g, the theoretical weight of $BaSO_4$ obtainable from the amount of reactants used.

As a general rule, the amount of soluble material adsorbed is roughly proportional to its concentration. The data in Table 8.5 for the precipitation of sulfuric acid with barium chloride in the presence of potassium nitrate[19] show the variation in weight of barium sulfate formed under different conditions. The calculated weight of barium sulfate which should have been obtained was 1.0118 g. In view of the above statement,

[18] Balarev, *Z. anal. Chem.* **102,** 241 (1935); *Koll. Beih.* **50,** 1 (1939).
[19] Blasdale, *Fundamentals of Quantitative Analysis,* p. 138, Van Nostrand, 1936.

precipitations should be made preferably from very dilute solutions in order to reduce the concentration of the contaminant. However, there are two practical limitations to carrying the dilution too far: (1) very dilute solutions are ideal for preparing colloidal dispersions; and (2) large volumes of solution take too much time for filtration and may result, also, in excessive loss from solubility.

Most entrainment probably takes place during the course of the formation of the precipitate. If the same amount of barium sulfate is precipitated in the presence of potassium nitrate, or is first precipitated and then put in the nitrate solution, the first preparation will show by far the greater error.

The method of precipitation may be important. Thus, adding the precipitant slowly to a stirred, fairly dilute solution may aid in prevention of entrainment in some cases.

Sometimes the order of mixing is significant, i.e., whether A is added to B, or vice versa. Barium sulfate precipitated by adding sulfuric acid to the solution of barium chloride has a better physical state than the product resulting from a reversal of the process. If barium chloride, which is in excess in the first method, is adsorbed by barium sulfate, the weight of residue obtained is too small unless the residue has been treated with sulfuric acid and re-ignited.

Entrainment is often a selective process. Thus, potassium is adsorbed more than sodium by barium sulfate, and nitrate more than chloride.

Whenever entrainment is a surface phenomenon and other conditions are comparable, amorphous and finely divided precipitates adsorb more than other types of precipitates, owing to the greater surface area of the former.

Digestion of a precipitate often decreases entrainment errors; however, the effect may be just the opposite, especially if substances are present which tend to postprecipitate on the precipitate present.

Uniunivalent ions are likely to be least entrained, and uniunivalent salts are likely to entrain other substances least.

Avoidance of Entrainment Errors

Generally the errors resulting from entrainment are positive, i.e., the substance weighed is too heavy. In such cases, the residue weighed contains the expected substance, along with some impurity. Although negative errors are less frequent, two possible negative errors are of interest. Mention has been made already of the entrainment of some barium chloride when barium sulfate is precipitated with sulfuric acid. Negative error might also result if any adsorbed substance reacted on ignition to

form a volatile substance with constituents of the desired precipitate or residue.

Since the prediction of the extent of entrainment is impossible, care should be taken to avoid the difficulty as far as possible. There are several practical methods for such avoidance. The use of reasonably dilute solutions, as already mentioned, is of value if the entrainment is relatively small and the solubility of the precipitate is also small. A second method, double precipitation, depends upon the general proportionality between concentration and extent of adsorption. In this case the first precipitate is washed a few times, dissolved, and reprecipitated. The material entrained by the first precipitate will be very much less concentrated at the time of the second precipitation, and therefore adsorbed in much smaller amount. Reprecipitation is a common practice in handling strongly adsorbing precipitates which may be dissolved easily, such as hydrous ferric oxide and calcium oxalate. This principle is applied in the method in Chapter 31 for the analysis of limestone.

When the precipitate is one not easily dissolved, such as barium sulfate, removal of the adsorbable constituent before precipitation may be necessary. Evaporation serves to remove some substances. Since nitrate ion is adsorbed more than chloride ion, repeated evaporation with hydrochloric acid may be used for removal of the nitrate ion.

In other instances precipitation may be employed. A good example of this procedure is the determination of sulfate and iron in ferric alum, $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24\ H_2O$. If the sulfate ion is precipitated as barium sulfate, iron will be adsorbed and will produce a brown residue on ignition. The iron may first be precipitated as the hydrous oxide, $Fe_2O_3 \cdot xH_2O$. Since this precipitate has marked adsorptive capacity, it must be dissolved and reprecipitated. The sulfate may then be precipitated in the combined filtrates. There is another, more interesting, procedure. The iron is first precipitated as the hydrous oxide, and then, in the same vessel, the sulfate is precipitated. Hydrochloric acid is then added carefully, in an amount just sufficient to dissolve the iron precipitate. Any sulfate retained by the hydrous oxide will thus become available to react with the excess precipitant for the sulfate. Still another possibility is reduction of the ferric iron to the ferrous state before precipitation of the barium sulfate. This technic minimizes the error, since ferrous iron is adsorbed much less than ferric iron in this case. A more recent technic is to remove the iron by passing the solution through a cation exchange resin, as Dowex 50.

Often the impurity cannot be removed from the precipitate before weighing, in which case the contaminated residue is weighed and the

amount of contaminant is later determined and correction made. In the determination of silica in limestone (Chapter 31), the precipitate of hydrous silica is usually contaminated with iron, and often other substances. Ignition of the residue of impure silica leaves a constituent such as iron as the oxide. The residue is then treated with hydrofluoric acid (plus a drop or two of sulfuric acid). All the silica is volatilized as fluosilicic acid or silicon tetrafluoride. Re-ignition of the remaining residue yields only the oxides of the contaminants, which may then be dissolved and added to the filtrate from the original silica filtration. The decrease in weight between the two ignitions gives the weight of silica.

REQUIREMENTS OF AN ANALYTICAL PRECIPITATE

To be suitable for quantitative separations, a precipitate should meet certain requirements, among which insolubility, separability, filterability, purifiability, ignitability, and reproducibility are probably most important.

The precipitate should be as nearly *insoluble* as possible. Table 8.6 contains data for a few of the commonly used compounds. Low solubility is undoubtedly important, but this property alone may not be the controlling factor in selecting a precipitation form. Thus, silver iodide is less soluble than the chloride; but the latter is practically always used, even in atomic weight work, on account of its other more desirable properties. For example, the chloride is photochemically more stable.

The final solubility of a precipitate depends upon a number of factors, among which are the specific nature of the compound, the type of solvent used, the temperature of the solution, the particle size obtained, the

TABLE 8.6

SOLUBILITIES OF CERTAIN PRECIPITATES

Precipitate	*Temperature*	*Solubility* (in mg/l)	*Solubility Product*
$Al(OH)_3 \cdot xH_2O$	25	0.005	3.7×10^{15}
$BaSO_4$	18	2.5	1.1×10^{10}
$CaC_2O_4 \cdot H_2O$	25	6.7	2.6×10^{9}
CuSCN	18	0.48	1.6×10^{11}
$Fe(OH)_3 \cdot xH_2O$	18	4.8×10^{-9}	1.1×10^{-36}
$PbCrO_4$	18	4×10^{-5}	1.8×10^{-11}
$PbSO_4$	18	30.4	1.0×10^{-8}
$MgNH_4PO_4 \cdot 6\,H_2O$	25	137	2.3×10^{13}
AgI	25	0.002	1.0×10^{-16}
AgBr	25	0.124	4.3×10^{-13}
AgCl	18	1.5	1.1×10^{10}

common- and diverse-ion effects, complex formation, and the *p*H of the solution. Obviously, the over-all situation may not be simple.

Ideally, the precipitate desired, and that only, will separate. More realistically, the precipitate should be subject to as little entrainment as possible.

The precipitate should be readily filterable. This requirement implies that the particle size of the digested precipitate should be sufficiently large that a rapid, large-pore filter medium can be used, and that the precipitate should not be easily peptized. Particle size is often controlled largely by the speed of formation of the precipitate.

The precipitate should be of such a nature that it can be freed of contaminants by washing with water or some solution, with the aid, if necessary, of dissolution and reprecipitation. Not all analytically useful precipitates, of course, can be dissolved prior to reprecipitation.

The effect of the *washing medium* on the precipitate must be carefully considered. Not only must it remove foreign material, but also it must not cause loss of precipitate through dissolution, chemical action, or peptization. Excess washing medium must be volatile at the temperature used for drying or igniting the precipitate.

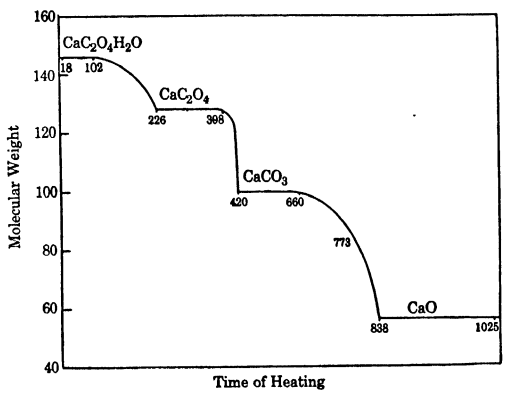


Figure 8.2

Weighing forms for a precipitate of calcium oxalate heated at different temperatures.

The precipitate, if it is to be measured gravimetrically, should be susceptible to drying or ignition as such, or be convertible to some other form of definite and known composition. Thus, silver chloride can be dried at 110° and barium sulfate ignited at 900° without decomposition.

In contrast, calcium oxalate, $CaC_2O_4 \cdot H_2O$, is generally ignited at 550° to convert it to the carbonate, $CaCO_3$, or at 900° to convert it to the oxide, CaO. The former weighing form is preferable from the standpoint

of stability. Calcium oxide readily absorbs carbon dioxide and/or water vapor from the air.

Duval[20] and his associates have reported an extensive series of studies on the thermal stability of different weighing forms for a large number of precipitates. The curve in Figure 8.2 shows these thermolysis results for calcium oxalate, $CaC_2O_4 \cdot H_2O$. The several horizontal sections indicate the following possible weighing forms, and the appropriate temperatures for heating:

$$CaC_2O_4 \cdot H_2O, < 100°; CaC_2O_4, 350°; CaCO_3, 550°; \text{and } CaO, > 850°.$$

Knowledge of the weight relation between the desired constituent and the product weighed is essential. Although it need not be stoichiometric, it must be reproducible. Ammonium molybdophosphate, $(NH_4)_3[P(Mo_3O_{10})_4]$, is a quantitative separating form for phosphorus, but its over-all composition is too uncertain for weighing as such.

The precipitate, if to be measured by volume, must form in reproducible physical state. The difficulty of meeting this requirement probably accounts for the small use made of such measurements.

SELECTION OF PRECIPITANTS

With a wealth of substances available as possible precipitants, the analyst faces the problem of selecting the best one for a given purpose. The list comprises chiefly compounds, most of which are inorganic acids, bases, and salts, and organic substances of various kinds.

Requirements of a Precipitant

As a guide to intelligent selection of a precipitant, our first interest is the nature of the specific requirements for such reactants. Obviously, the ideal precipitant should yield a product that meets the requirements for precipitates. In addition, the reagent should possess other properties, the most important of which are summarized below.

The cost should be reasonable. Use of expensive chloroplatinic acid to precipitate potassium, for example, necessitates work and expense in collecting and re-working the residue to recover the platinum.

Ready availability of the reagent is highly desirable. Occasionally, application of a meritorious reagent is delayed considerably because of its scarcity.

Preferably, the substance should be soluble in water. The ethanolic solution of dimethylglyoxime, long used to precipitate nickel, is objectionable because much excess of precipitant results in contamination of the

[20] See *Anal. Chem.* **23**, 1271 (1951) for a review of methods and results of this work.

nickel complex with dimethylglyoxime itself. Probably next best to water as a solvent are common acids and alkalies, if they are not themselves objectionable in the system in which the precipitant is to be used.

Long-time stability of the reagent is desirable. Instable systems must be watched. In the first place, decomposition may simply deplete the solution of the desired reactant, so that then a given volume does not accomplish the expected result. In the second place, some reaction within the solution may contribute an undesirable substance to the system being analyzed; two common examples of this reaction may be mentioned. (1) Aqueous ammonia acts on common glassware containers to produce the familiar siliceous "flakes" that, unless filtered out, contribute insoluble matter to the system; (2) solutions of ammonium oxalate should be prepared fresh to precipitate calcium, since old solutions may contain some carbonate, which then yields a mixed precipitate of oxalate and carbonate. This result ruins the precipitate for titrimetric or colorimetric measurement of the calcium.

From the viewpoint of selectivity, the analyst desires a precipitant that will react with the constituent he wants, and with that constituent only. Since such an ideal reactant is thus far out of the question, he strives for as high selectivity as possible. Many individual examples of achievement in this direction might be cited, but no particularly useful generalizations yet seem possible.

Efforts to increase the selectivity or specificity of chemical reagents, which would decrease the necessity of separations, have been largely in the direction of finding reagents which react with fewer substances. Feigl and others have had considerable success with selective organic reagents. Combined with this search has been extensive study of the possibilities of avoiding undesirable reactions through the formation of inactive complexes[21] of possible interferers. This was mentioned in Chapter 5.

Types of Precipitants

In general, the common inorganic precipitants are acids, such as hydrochloric and sulfuric, hydrogen sulfide, aqueous ammonia, hydrogen peroxide, and salts, principally of ammonia.

Various considerations enter into the selection of one of these types. Perhaps the most important is the volatility of the excess precipitant that might be retained by the precipitate. Obviously, ammonium salts are preferable in most cases to those of sodium or potassium.

[21] Such complexants have been referred to by some writers as "masking" or "sequestering" agents. The common connotations of these words make such usage doubtful.

Much work has been done in the past few decades on organic precipitants. The classic example, of course, is the use of dimethylglyoxime (biacetyldioxime) for nickel, especially in steel analysis. The discovery of the action of this compound by Tschugaev in 1905 probably marked the beginning of such applications of organic reagents. A few of the well-known reactants are summarized in Table 8.7.

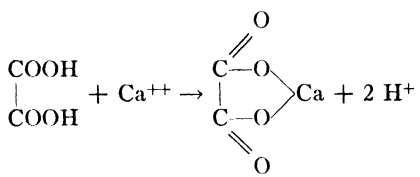
TABLE 8.7

SELECTED ORGANIC PRECIPITANTS

Precipitant	*Empirical Formula*	*Examples of Ions Precipitated*
Benzidine	$C_{12}H_{12}N_2$	SO_4^{--}
Cupferron	$C_6H_9O_2N_3$	Fe^{+++}, TiO^{++}, ZrO^{++}, UO_2^{++}
Dimethylglyoxime	$C_4H_8O_2N_2$	Ni^{++}, Pd^{++}
Nitron	$C_{20}H_{16}N_4$	NO_3^-, ClO_4^-
Oxine (8-quinolinol)	C_9H_7ON	Al^{+++}, Mg^{++}, Zn^{++}
Phenylarsonic acid	$C_6H_7O_2As$	ZrO^{++}
Salicylaldoxime	$C_7H_7O_2N$	Cu^{++}

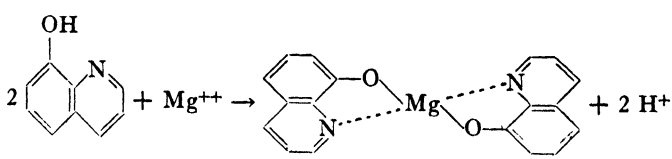
The reaction of many such organic compounds with inorganic ions takes place through functional groups of the precipitant. Two types of action may be illustrated with oxalic acid and with oxine (8-quinolinol).

Oxalic acid reacts with calcium ion according to the equation



although few texts formulate the mechanism in this way. The calcium oxalate does not precipitate, of course, until the acidity is adjusted, usually with ammonium hydroxide, to a *p*H about 6. Such a process is usually referred to as salt formation, and the bonds are electrovalent.

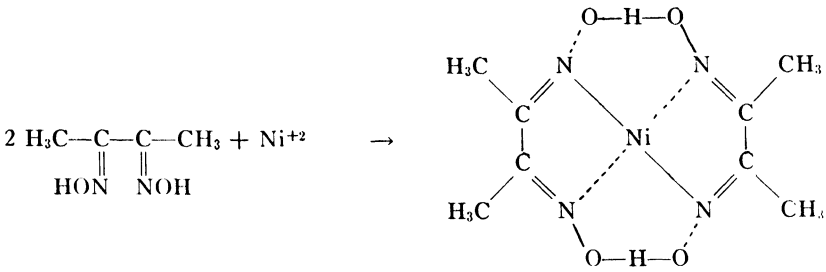
Mixed electrovalent and co-ordinate bonding is involved in the reaction of oxine with magnesium ion according to the equation



The metal-containing rings so formed are often referred to as chelate

rings. This type of reaction is very common, both here and in the formation of colored complexes employed in colorimetric methods.

A better-known reaction of this second type is that of nickel (II) ion with dimethylglyoxime, according to the equation



An interesting development is precipitation in homogeneous solution, a technic largely pioneered by Willard.[22] This process involves generating the precipitating agent *in situ*. Usually this is accomplished by a hydrolytic reaction which produces the desired reagent by the hydrolysis of a noninterfering substance. Thus, the sulfate ion required for precipitation of barium ion as barium sulfate can be supplied by the hydrolysis of dimethyl sulfate, the equation for the reaction being[23]

$$(CH_3)_2SO_4 + 2\ H_2O \rightarrow H_2SO_4 + 2\ CH_3OH$$

Since such a process involves essentially the molecular addition of the reagent uniformly throughout the reaction medium, instead of the conventional method of adding the reagent solution to the reaction solution, the result is a more nearly pure precipitate. In addition, because of the slow rate of precipitation, the particles obtained are considerably larger and, consequently, more readily filtered than those obtained by the conventional method of precipitation.

In the usual procedure the precipitant solution is added dropwise to the sample solution. At the point where the drop of reagent enters the solution, there is momentarily present, even with the most efficient stirring, a relatively large excess of the reactive ion, which may result in the precipitation of substances present in the sample that would normally be soluble in the mixture of the sample and reagent solutions. This local excess may cause contamination of the coprecipitation type. In the ordinary procedure for precipitating barium ion by the addition of sulfuric acid, even small amounts of calcium, of the order of a few milligrams, contaminate the barium sulfate by coprecipitating calcium sulfate. Hydrol-

[22] *Anal. Chem.* **22**, 1372 (1950).
[23] Elving and Van Atta, *ibid.*, 1375 (1950).

ysis of dimethyl sulfate, however, will precipitate barium free of contamination in the presence of more than 100 times as much calcium.

The use of *p*H to control selective precipitation of hydroxides and basic salts has long been practiced. More work may extend the fractional precipitation of other salts. An interesting, and possibly highly useful technic based on stepwise precipitation, has been described under the name of "riptographic analysis."[24] The separations potentially available through hydrolytic precipitation have been well summarized by Gilchrist.[25] Included is the possible analytical separation of some 40 of the chemical elements.

Another recently developed precipitation method is based upon the demonstration that urea possesses the interesting property of forming solid complex compounds with straight-chain organic compounds. These solid urea adducts can be used to effect the separation of straight-chain compounds from their isomeric branch-chain compounds.

Applicability

In applied analysis another consideration is often of great importance in the selection of a precipitant. Selection is governed by what is to be done with the filtrate left from the precipitate. The first possibility is simply to discard the filtrate. If one were determining lead in such a case, and if no interfering constituent were present, the precipitate produced might well be the sulfate, sulfide, carbonate, oxalate, chromate, molybdate, or perhaps others. The various compounds formed are not all equally satisfactory precipitation or weighing forms; but at least the use of some excess precipitant, in the form of the acids or the ammonium salts, is not a problem.

The second possibility is much more involved. It occurs in cases of polycomponent analysis where one component after another is removed by precipitation. If an analyst were determining, by this method, the lead in a solution containing also chromium and molybdenum, addition of chromate or molybdate to precipitate the lead would be ruinous.

In this type of work, therefore, selection of the precipitant must be made with such possibilities uppermost in mind. An attempt to avoid such complications accounts largely for the use of a reagent, an excess of which may be removed easily by boiling, evaporation to dryness, or some simple chemical reaction. The excess of some organic precipitants, for example, may have to be removed by evaporation with nitric acid.

[24] Toffoli, *Gazz. chim. ital.* **68**, 277 (1938); **74**, (1944).
[25] *J. Research Nat. Bur. Standards* **30**, 89 (1943).

APPLICATIONS OF THE PRECIPITATION METHOD

Precipitation is one of the oldest and most frequently used separation technics. Because of the stress long placed on it in elementary courses and because of its historical position, it has almost come to symbolize what some call "old-fashioned" analysis.

The classical methods of inorganic qualitative analysis are based primarily upon the possibility of separating the elements, in the form of certain kinds of compounds, by precipitating these compounds. The importance of precipitation as a separative process is amply illustrated by the success achieved in classical chemical analysis by the systematic procedure for the analysis of a silicate or carbonate rock. The efficiency of separation by any technic has rarely been as high as that achieved in the scheme of rock analysis described by Washington or Hillebrand and Lundell.[26] Lundell and Hoffman[27] outline a general inorganic quantitative separative scheme for the elements, based upon precipitation separations.

One does not necessarily precipitate a given element or radical in the same form for qualitative and quantitative determinations. Often in quantitative work one of several precipitation forms may be selected, as mentioned for lead in the previous section.

Some elements form no compounds sufficiently insoluble for quantitative separations; or, if the compounds have the required degree of insolubility, some other property prevents their being used quantitatively. The insoluble yellow complex ammonium molybdophosphate is an example of a precipitate which is quantitative but which cannot be ignited to a definite form. After separation, therefore, it must be dissolved and reprecipitated as magnesium ammonium phosphate if the phosphate is to be measured gravimetrically.

The large number of cases in which precipitation methods are used as a means of separation is shown by reference to standard, comprehensive treatises in analytical chemistry.[28] Such works include these methods chiefly under gravimetric methods of measurement.

Most precipitation methods of separation, if they are considered applicable (and they are widely applicable), are reasonably good from the standpoint of being quantitative, particularly when advantage may

[26] Washington, *The Chemical Analysis of Rocks,* Wiley, 1930; Hillebrand, Lundell, Bright, and Hoffman, *Applied Inorganic Analysis,* Wiley, 1953.

[27] Lundell and Hoffman, *Outlines of Methods of Chemical Analysis,* Wiley, 1938.

[28] Hillebrand, Lundell, Bright, and Hoffman, *loc. cit.;* Furman, *Scott's Standard Methods of Chemical Analysis,* Van Nostrand, 1939; Fresenius and Jander, *Handbuch der analytischen Chemie,* Springer, 1940.

be taken of the common-ion effect. The cost of precipitation is usually low, both for equipment and service and for reagents, except in a few cases where platinum ware or expensive reagents are used.

Several disadvantages are apparent. Both time and care are required to make successive, accurate separations for substances such as limestone. Good work demands thought, skill, and knowledge beyond the mere ability to read a set of directions and to execute the operations described.

Students frequently gain the impression that determinations involving precipitation separations and gravimetric measurement are superior in accuracy to those based upon titrimetric measurements. In some instances this is true, but in many it is not. Many atomic weight determinations are based upon handling silver chloride, but the utmost precautions are employed; on the other hand, many precipitation-gravimetric determinations by beginning students often may be seriously in error.

CHAPTER 9

SEPARATION BY ELECTROCHEMICAL PROCESSES

A number of separations, usually of metals, can be made by electrochemical methods. Two processes of accomplishing electrochemical separations are described here: (1) *electrodeposition,* in which the separation is made by means of an externally applied potential; and (2) *displacement,* in which one element is displaced by another higher in the electromotive force series. The former of these two methods is by far the more commonly used.

Before attempting to discuss these methods of separation, it is desirable to review and extend certain facts concerning electricity and electrochemical behavior that were probably discussed in previous courses in chemistry and physics.

For additional discussion of electrochemical processes, the student may wish to consult the literature. The nature and use of electrodeposition methods have been surveyed by Sand,[1] and recent developments have been summarized by Ashley.[2]

Fundamental to any discussion of electrochemistry are Faraday's two laws of electrolysis. The first law states that *the amount of substance liberated at an electrode in unit time is proportional to the intensity of the current.* This means that the greater the amperage indicated by a meter connected in the electrical circuit, the more material will be deposited on the electrode in a given period of time. The second law states that *the amounts of different substances deposited in the same period of time by the same current are proportional to their chemical equivalent weights.* Experiments based on the second law have proved that 96,500[3] coulombs of electricity (1 faraday) are required to

[1] *Electrochemistry and Electrochemical Analysis,* 3 vols., Blackie, 1940. See also Lingane, *Electroanalytical Chemistry,* p. 163, Wiley, 1954.

[2] *Anal. Chem.* **21,** 70 (1949).

[3] The value 96,492 ± 3 is reported by Craig and Hoffman, *Nat. Bur. Standards Circ.* **524** (1953).

transport or react with 1 gram-equivalent weight of an element or compound. A current efficiency of 100 per cent is a prerequisite here, of course.

The behavior of the electrical components in a closed circuit involving direct current is summarized in Ohm's law. This generalization states that the current intensity is equal to the applied potential divided by the resistance in the circuit. Usually the current I is given in amperes; the applied potential E (sometimes called voltage or electromotive force, emf) is given in volts; and the resistance R is given in ohms. Ohm's law is then

$$I = \frac{E}{R} \quad \text{or} \quad E = IR$$

The nature of these electrical units of measurement follows.

The unit of resistance is the *ohm*. It is defined as the resistance offered to a constant current by a column of mercury 14.452 g in mass, 106.300 cm in length, at 0°, and of constant cross-section.

The unit of current is the *ampere*. It is defined as the current that will cause the deposition of 0.001118 g of silver from a solution of silver nitrate in 1 sec.

The unit of quantity of electricity is the *coulomb*. It is the amount passed when a current of 1 amp. flows for 1 sec. The coulomb is the capacity factor of an electric current.

The unit of electromotive force, or difference in potential, is the *volt*. It is the electromotive force necessary to drive a current of 1 amp. through a resistance of 1 ohm. The volt is the intensity factor of an electrical current.

Electrodeposition Separations

In the majority of electrochemical separations the essential reaction is effected by means of a direct electrical current passed through a solution containing the desired constituent in ionic form. In the case of cations the process consists in reduction through the addition of electrons at the cathode, the separation of copper being the most familiar example.[4] The much less commonly used process of oxidation involves removal of electrons at the anode, as in the separation of the halogens as halides on a silver electrode.

The term "electrolytic" is used most often in connection with such

[4] Copper was the first element so separated. Oliver Wolcott Gibbs reported the work in 1864.

methods. Usually, however, it is used to refer to the whole procedure rather than merely to the method of separation.

Phenomena of Electrolysis

In considering the nature of the process of quantitative electrodeposition certain facts of electrolysis upon which such separations are based must be discussed.

1. In the apparatus for making electrodepositions are two kinds of electrical conductors, on which the passage of current has different effects. In the *wires, electrodes,* and *instruments* the passage of current produces no permanent alteration in their nature. On the other hand, in the *solution* electrolyzed there is a permanent change. These solutions usually contain acids, bases, or salts dissolved in water.

2. The conducting solutions contain electrically charged ions, which serve as a means of conducting the current.

3. The conducting ions move to the oppositely charged electrodes during the passage of a direct current, as in electrolysis. Positively charged cations, such as copper, go to the negatively charged cathode; negatively charged anions, such as the chloride ion, go to the positively charged anode.

4. The ions, on reaching the electrodes, lose their electric charge, and, consequently, at the same time lose the properties which characterize them as ions. Some, such as silver, are deposited on the electrode, where they adhere; some, such as chloride, are largely evolved from the solution as a gas.

5. Under certain conditions, some of these products can be deposited quantitatively on a solid electrode, such as platinum, or in a liquid electrode, such as mercury, and measured. A gaseous product can, of course, be measured.

Chemical Changes Effected by the Electric Current

When a current is passed through a solution of an electrolyte, definite kinds of chemical action are produced. At the cathode there is an addition of electrons, which results in a reduction of the positively charged ions. For cupric and hydrogen ions the reactions are represented by the equations

$$Cu^{+2} + 2\,e \rightarrow Cu \text{ (metal)}$$
$$2\,H^{+} + 2\,e \rightarrow H_2 \text{ (gas)}$$

At the anode there is a removal of electrons, which results in an oxidation of the negatively charged ions. For the chloride and hydroxide ions the reactions are represented by the equations,

$$2\ Cl^- \rightarrow Cl_2\ (gas) + 2\ e$$
$$4\ OH^- \rightarrow 2\ H_2O + O_2\ (gas) + 4\ e$$

The products which may result from the passage of an electrical current through an aqueous solution frequently depend upon several factors. Every aqueous solution contains hydrogen and hydroxide ions, in addition to those contributed by the solute. A solution of cupric nitrate, for example, contains at least cupric, hydrogen, nitrate, and hydroxide ions. All such ions probably exist in a solvated (i.e., hydrated) state. What products result from electrolysis of this system? Under suitable conditions of potential and current, copper will be liberated and deposited on the cathode, and oxygen will be liberated at the anode. In each case the ion reacting at the electrode is the one requiring the least energy to discharge it. As the cupric and hydroxide ions are used up, the hydrogen ion, and hence the acidity, increases.

Conditions Affecting Electrolytic Separations

We may now examine in greater detail conditions that control and affect electrodepositions. The most obvious of these conditions are the magnitude of the electromotive force, or potential difference, applied to the solution, i.e., the *voltage,* and the magnitude of the current passing through the solution, i.e., the *amperage.*

VOLTAGE RELATIONS IN ELECTROLYSIS

Any consideration of the current conditions, as they concern voltage and amperage, must take into account the relationship of current, potential, and resistance, as expressed in Ohm's law, $I = E/R$. Voltage measures the emf of the current impressed upon the system electrolyzed. We are interested in the limits within which it may vary.

In the direction of maximum voltage, if the analyst is separating a single element such as copper from a solution of the nitrate, there is probably no limit, except as excessive voltage might raise the amperage too much (as noted later). This statement does not apply to systems where two or more elements are present that might be deposited simultaneously if the voltage were high enough. This reservation is amplified in the discussion on applications.

In the direction of minimum voltage, there is a definite lower limit known as the *decomposition voltage.* It is defined as the minimum voltage (measured across the electrodes) below which no decomposition takes place and no electrolysis can proceed continuously.

Observation has shown that continuous deposition results only when the applied emf is somewhat greater than the sum of (1) the voltage

necessary to overcome the electrical resistance of the solution, (2) the back emf of the system, and (3) the overvoltage. Each of these three factors will now be considered.

Solution resistance. The solution offers a certain resistance to the passage of an electric current through it. Although the resistance offered by metals such as those used in the wires, connections, and electrodes, is very low, that offered by the solution is appreciable. In general, the resistance of the solution increases as the concentration of ions in it decreases.

If R is the resistance in ohms and I the current in amperes, Ohm's law indicates that the voltage required to overcome the electrical (ohmic) resistance is given by the relationship $E = IR$. This fall in potential in overcoming the solution resistance is often referred to as the IR drop of the solution.

Back emf. The back electromotive force results from the tendency of the substances deposited on the electrodes to act as sources of potential, i.e., as batteries or cells. The back emf, strictly speaking, consists of two parts: the reversible emf and the overvoltage. The latter is considered separately in a subsequent section. Pursuance of the inquiry as to why there is a reversible emf leads to the subject of *electrode potentials.*

That a difference of potential exists between a metal and a solution of its ions with which it is in contact is known. A strip of zinc dipping into water is believed to go into solution slightly, because of electrolytic solution pressure, with the formation of zinc ions. The process will not proceed far, but will continue until an equilibrium is established according to the equation

$$Zn \rightleftarrows Zn^{+2} + 2\,e$$

The metal is then charged negatively, assuming the electrons accumulate upon it, and the solution is charged positively by the zinc ions. The more dilute the solution with respect to zinc ions, the greater the potential developed. The general reaction for metals is represented by the equation

$$\text{Metal} \rightleftarrows \text{ions} + \text{electrons}$$

and for nonmetals it is,

$$\text{Nonmetal} + \text{electrons} \rightleftarrows \text{ions}$$

Many elements, including metals and such nonmetals as chlorine and oxygen, have been studied to determine the potential difference existing between them and a solution of their ions. Nernst deduced an equation[5]

[5] See textbooks on physical chemistry for derivation of the Nernst equation.

relating the potential difference, set up at the contact between an element and a solution of its ions, to the concentration of the ions involved. If we consider the reaction taking place at the electrode as a reversible oxidation-reduction process, the statement of the equation becomes

$$\text{Reduced form} \rightleftarrows \text{oxidized form} + n \text{ electrons}$$

The potential E at the electrode is given by the generalized form of the Nernst equation

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}}$$

in which E is the observed potential; E^0 is the standard electrode potential prevailing when the activity of the reduced form a_{red} equals that of the oxidized form, a_{ox}; n is the number of electrons lost or gained; R is the molar gas constant (8.316 volt-coulombs per degree); T is the absolute temperature; and F is the faraday (96,500 coulombs). Usually the equation is written in decimal logarithms at a standard reference temperature of 25°. If concentrations are substituted for activities, the equation becomes

$$E = E^0 - \frac{0.0591}{n} \log \frac{[ox]}{[red]}$$

Applying the equation to a zinc electrode, we have,

$$E = E^0_{Zn} - 0.0295 \log \frac{[Zn^{+2}]}{[Zn]}$$

in which [Zn] represents the concentration of the reduced form, i.e., the metal itself. Since the metal is only slightly soluble, this value may be considered as a constant and included in the E^0 value. The equation then becomes

$$E = E^0_{Zn} - 0.0295 \log [Zn^{+2}]$$

The letter C is sometimes used [6] instead of the symbol for the individual ion.

Two conventions are employed in chemistry for writing electrode potential expressions. One is the form already used, which corresponds in the general case to

$$M^{+(m-n)} \rightleftarrows M^{+m} + n\,e$$

and

$$E = E^0 - \frac{0.0591}{n} \log \frac{[ox]}{[red]}$$

[6] C represents concentration in moles per liter. The effective concentration is obtained by multiplying the concentration by the activity coefficient. In this discussion concentration in moles per liter is considered a sufficiently accurate approximation.

Physical chemists have come more and more to use this form because of its basis in thermodynamic theory.

According to the other convention, the general equation is

$$\text{Ox} + n\,e \rightleftarrows \text{red}$$

whence the Nernst expression becomes

$$E = E^0 - \frac{0.0591}{n} \log \frac{[\text{red}]}{[\text{ox}]}$$

The only essential difference between the two statements is that the standard electrode potentials E^0 have opposite signs in the two systems although the numerical values are identical. Either system may be used, but any attempt to use both systems on the same problem will result in contradiction and inconsistency.

Electrode potentials. Experimental determination of standard electrode potentials has yielded data upon which the familiar emf series of elements is arranged. Table 9.1 gives electrode potentials for some of the elements.

The standard electrode potential is the potential of a given reversible

TABLE 9.1

LIST OF SELECTED STANDARD ELECTRODE POTENTIALS AT 25°

Half-cell Reaction	*Standard Electrode Potential* (in volts)
$Li \rightleftarrows Li^+ + 1e$	3.02
$K \rightleftarrows K^+ + 1e$	2.92
$Ca \rightleftarrows Ca^{++} + 2e$	2.87
$Na \rightleftarrows Na^+ + 1e$	2.71
$Mg \rightleftarrows Mg^{++} + 2e$	2.34
$Al \rightleftarrows Al^{+++} + 3e$	1.67
$Zn \rightleftarrows Zn^{++} + 2e$	0.76
$Fe \rightleftarrows Fe^{++} + 2e$	0.44
$Cd \rightleftarrows Cd^{++} + 2e$	0.40
$Co \rightleftarrows Co^{++} + 2e$	0.28
$Ni \rightleftarrows Ni^{++} + 2e$	0.25
$Sn \rightleftarrows Sn^{++} + 2e$	0.14
$Pb \rightleftarrows Pb^{++} + 2e$	0.13
$H_2 \rightleftarrows 2\,H^+ + 2e$	0.00
$Cu \rightleftarrows Cu^{++} + 2e$	−0.34
$Ag \rightleftarrows Ag^+ + 1e$	−0.80
$Hg \rightleftarrows Hg^{++} + 2e$	−0.85
$2\,H_2O \rightleftarrows O_2 + 4\,H^+ + 4e$	−1.23
$2\,Cl^- \rightleftarrows Cl_2 + 2e$	−1.36
$Au \rightleftarrows Au^{+++} + 3e$	−1.42

electrode system, such as

$$\text{Red} \rightleftarrows \text{ox} + n\,e$$

when the ions involved have unit activity and any gases involved have a pressure of 1 atm. The requirement of unit activity is only approximately equivalent to a concentration of 1 gram-ion per liter for each ion in the system.

In theory, at least, the data in Table 9.1, or other data calculated from the Nernst equation, could be used for selection of elements to arrange a voltaic cell for the production of electrical energy. Zinc and copper, for example, are used in the Daniell cell. In it the chemical process proceeds according to the equation

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$$

The standard potential of zinc is +0.76 and that for copper is −0.34 volts. The algebraic difference between these values, 1.10, is the voltage of the cell.

If a solution such as zinc chloride is electrolyzed at sufficient voltage (i.e., above the decomposition voltage), zinc is deposited on the cathode and chlorine is liberated at the anode. The potential at the cathode has been considered already. At the anode the potential is given by the expression

$$E = E^0_{Cl_2} - 0.0591 \log \frac{[Cl_2]^{1/2}}{[Cl^-]}$$

If the solution contained nitrate or sulfate ions instead of chloride ions, oxygen would be liberated at the anode and the potential would be given by the expression ($2\ OH^- \rightleftarrows H_2O + \frac{1}{2}\ O_2 + 2\ e$),

$$E = E^0_{O_2} - \frac{0.0591}{2} \log \frac{[O_2]^{1/2}}{[OH^-]^2}$$

Since

$$K_w/[H^+] = [OH^-]$$

$$E = E^{0\prime}_{O_2} - \frac{0.0591}{2} \log \frac{[O_2]^{1/2}}{K_w^2} - \frac{0.0591}{2} \log [H^+]^2$$

On elimination of the constants K_w and $[O_2]$, and simplification, the equation becomes

$$E = E^0_{O_2} - 0.0591 \log [H^+]$$

or

$$E = E^0_{O_2} + 0.0591\ p\text{H}$$

Reference to Table 9.1 shows that the oxygen potential is −1.23 volts in a solution that is molar with respect to hydrogen ions.

Whenever a solution is electrolyzed, therefore, the products liberated at the electrodes set up a voltaic cell. Thus, the products for a solution

of cupric nitrate would be copper at the cathode and oxygen at the anode. Discontinuance of the external current will furnish momentarily a copper-oxygen cell. For a solution molar with respect to these constituents, the decomposition voltage would be 0.89, since the molar electrode potentials are −0.34 for copper and −1.23 for oxygen. In order to have continuous deposition of copper from such a solution, the applied emf must exceed that of the decomposition voltage. The latter is the sum of these reversible potentials at cathode and anode, plus the *IR* drop in the solution, plus the overvoltage. On the basis of this reasoning alone, a solution of cupric sulfate of the same concentration should have the same decomposition potential as cupric nitrate, since the products are copper and oxygen in both cases. Nickel sulfate would be different, with nickel and oxygen as the products.

The electrolytic solution pressure of a metal varies with the concentration of its ions in the solution with which the metal is in contact, as shown in Figure 9.1. Consequently, we may expect a corresponding variation in the decomposition potential of this solution. Then as the concentration changes during electrolysis, the voltage necessary to maintain steady deposition must change also. The magnitude of this change may be predicted from the Nernst equation. For the concentration C, the expression is

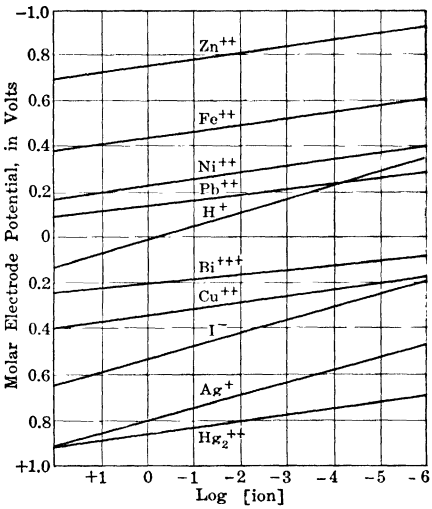


Figure 9.1

Effect of ion concentration upon electrode-electrolye potential.

$$E = E^0 - \frac{0.0591}{n} \log C$$

When this concentration is reduced to one-tenth the original value,

$$E = E^0 - \frac{0.0591}{n} \log \frac{C}{10}$$

$$= E^0 - \frac{0.0591}{n} (\log C - \log 10)$$

$$= E^0 + \frac{0.0591}{n} - \frac{0.0591}{n} \log C$$

TABLE 9.2

OVERVOLTAGE OF GASES ON METALLIC ELECTRODES*
(in volts)

	Hydrogen							*Oxygen*						*Chlorine*	
Current Density†	Ag	Au	Cu	Hg	Ni	Pt (smooth)	Pt (pltzd.)	Ag	Au	Cu	Ni	Pt (smooth)	Pt (pltzd.)	Pt (smooth)	Pt (pltzd.)
1	0.48	0.24	0.48	0.88	0.56	0.02	0.01	0.58	0.67	0.42	0.35	0.72	0.40	0.008	0.006
5	0.69	0.33	0.55	1.02	0.70	0.05	0.03	0.67	0.93	0.55	0.46	0.80	0.48	0.02	0.01
10	0.76	0.39	0.58	1.04	0.75	0.07	0.03	0.73	0.96	0.58	0.52	0.85	0.52	0.03	
50	0.83	0.51		1.06	0.89	0.19	0.04	0.91	1.06	0.64	0.67	1.16	0.60	0.05	0.02
100	0.87	0.59	0.80	1.07	1.05	0.29	0.04	0.98	1.24	0.66	0.73	1.28	0.64	0.09	0.03
200	0.94	0.67	0.99	1.08		0.36	0.04	1.04		0.69	0.77	1.34		0.16	0.04
500	1.03	0.77	1.19	1.10	1.21	0.57	0.05	1.08	1.53	0.74	0.82	1.43	0.70	0.21	0.05
1000	1.09	0.80	1.25	1.11	1.24	0.68	0.05	1.13	1.63	0.79	0.85	1.49	0.77		
1500	1.09	0.81	1.27	1.12	1.25	0.77	0.05	1.14	1.68	0.84	0.87		0.78	0.26	0.10

* See Knobel, Caplan, and Eiseman, *Trans. Am. Electrochem. Soc.* **43**, 55 (1923).

† In milliamps. per sq. cm.

When the concentration is reduced to one one-hundredth of the original concentration,

$$E = E^0 - \frac{0.0591}{n} \log \frac{C}{100}$$

$$= E^0 + \frac{0.0591}{n} (2) - \frac{0.0591}{n} \log C$$

Therefore, for each tenfold decrease in concentration, there is an increase of $0.0591/n$ volts (at 25°) in the electrode potential of the metal. It is evident that an infinite potential would be required to separate a metal completely.

Overvoltage. In practice a considerable difference between the voltage actually needed to maintain continuous deposition and that calculated from the standard electrode potentials and the potential drop in the solution is often observed. This difference is known as the overvoltage. Overvoltage results from polarization effects at the electrodes. The magnitude of the effect for metal deposited on metal is moderate or small (0.1 volt or less); for gases the effect is much greater. Table 9.2 shows some experimentally determined overvoltage values for different gases on various types of electrodes. Overvoltage depends upon many variables, including the nature of the substance liberated, the nature of the electrode surface, the previous treatment of the electrode surface, and the current density (amp. per sq. cm of electrode surface). With the uncertainties in actual operating conditions introduced by this factor, it is evident that calculations based on electrode potentials alone may be seriously in error.

Although overvoltage complicates the calculation of electrode potentials, its effect makes feasible certain separations otherwise impossible. For example, hydrogen is considerably below zinc and iron in the emf series, and its discharge should prevent the deposition of the metals. Actually, both metals can be separated quantitatively, zinc from a zincate complex and iron from an oxalate complex. It is of interest in the latter example to note that the overvoltage phenomenon seems inoperative at times, for no deposit of iron can be obtained. By using a mercury cathode, on which the overvoltage of hydrogen is high, the analyst may separate the alkali and alkaline earth metals which are far above hydrogen in the series.

Amperage Relations in Electrolysis

The amperage controls the rate of deposition in electrolysis, the material deposited in unit time being proportional to the intensity of the

current. The latter depends upon the rate at which the charges on the electrodes are renewed, i.e., upon the quantity of electricity that passes through the solution in unit time.[7]

Change of rate of deposition. The rate of deposition is changed by anything that affects the current density. Several factors may be mentioned.

According to Ohm's law[8] $I = E/R$, a change in the voltage E or in the resistance R will affect the current I. In addition to changes in the potential of the electrolyzing current itself, changes may be made in the current by varying factors that affect the resistance of the solution, such as the temperature and the distance between the electrodes used.

The rate of deposition decreases rapidly with decrease in concentration of the ion being discharged. Since there are fewer ions to react, they do not reach the electrodes so rapidly. Stirring the solution decreases the effect, however.

A decrease in the concentration of the metallic ion may be achieved by the formation of a complex ion containing the metal. Since the resistance of the solution is increased, this practice is desirable only if it is necessary in order to obtain suitable deposits, as in the deposition of silver from the complex cyanide ion $Ag(CN)_2^-$.

Desirable rate of deposition. In contrast to voltage, amperage has no lower limit except the analyst's patience. Generally, the slower the rate of deposition, the better will be the physical state of the deposit.

Although no upper limit of amperage can be calculated, there is a practical one in the permissible current density. Analysts often refer to current density as the current in amperes per 100 sq. cm of electrode surface. The term "normal density" (N.D.) is often used to indicate the proper current density for the separation of a given constituent in a satisfactory adherent form.

EQUIPMENT FOR ELECTRODEPOSITION

In methods of analysis involving electrodeposition, the measurement of the desired constituent does not concern any electrical quantity. The passage of a direct electrical current is equivalent to the use of a

[7] Faraday's law, relating the amount of material deposited to the current passed, should not be assumed to apply in quantitative separations, unless the products deposited are the sole species carrying the current. In coulometers, where the law applies, the concentration of the ion being discharged is relatively high, the current passed is low, and the total amount deposited is only a fraction of that present. In other words, every precaution is taken to have all the current carried by specific species.

[8] Ohm's law for electrolysis is $I = \frac{E_1 - E_2}{R}$, where E_1 is the impressed emf and E_2 is the back emf.

chemical precipitant in order to bring about a desired separation. Usually the separated substance deposits on a solid electrode, such as platinum, or in a liquid electrode, such as mercury. Considcration of the use of this technic brings us to several practical topics.

In order to make electrolytic separations it is necessary to have a source of direct current, an adjustable resistance, and a cell for electrolysis, including the electrodes. In addition, there must be measuring

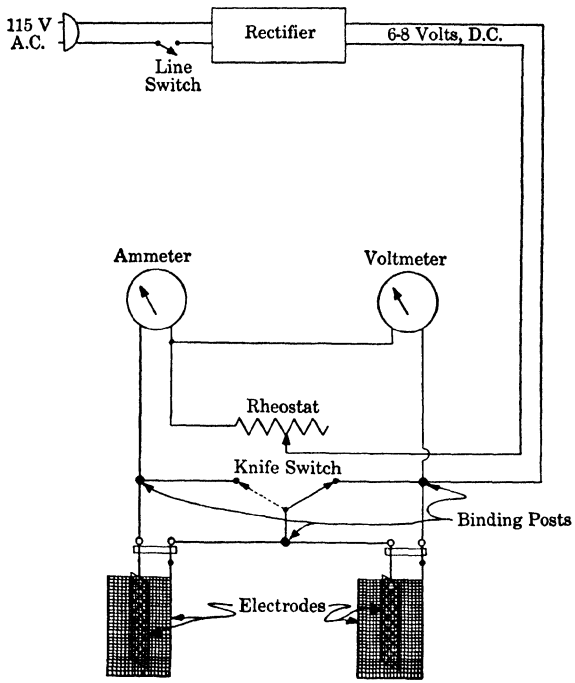


Figure 9.2

Essential electrical connection of student electrodeposition apparatus.

instruments if the current has to be controlled closely. Figure 9.2 shows the essential electrical connections for these items. The arrangement is designed for electrolyzing two solutions in series. When one cell is removed, the SPDT switch may be closed to allow the current to continue passing through the other cell.

Figure 9.3 shows a "homemade" apparatus incorporating the items illustrated for Figure 9.2. All wiring and component parts are visible.

These inexpensive units, made to operate with A.C. current, have been used in several laboratories.[9]

Figure 9.4 illustrates a commercial apparatus. Numerous types of such equipment are available for separations by electrodeposition.

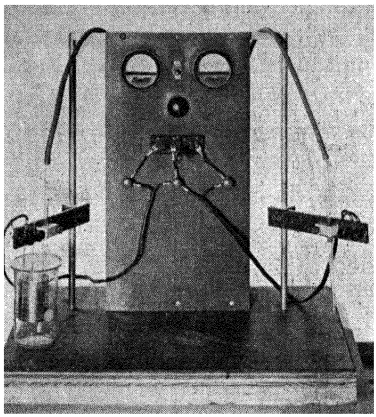


Figure 9.3

General view of student electrodeposition apparatus.

In all cases direct current is required as the source. It is provided most readily by storage batteries, since they are especially suited for giving a steady voltage, which is necessary to make certain separations. A small motor generator or rectifying unit, if equipped with adequate controls, may be used for most work by connecting it to the ordinary alternating current supply. The author's apparatus employs a rectifying unit. In some cases a battery booster or trickle charger unit is adequate.

The adjustable resistance is an ordinary rheostat of suitable capacity. The measuring instruments are most useful if they have two ranges. Useful ranges are 0 to 2 and 0 to 20 for the voltage, and 0 to 1.5 and 0 to 15 for the amperage.

For the electrolytic cells tall-form beakers are usually used. Preferably, the diameter is such that the cathode just fits inside easily. During electrolysis the beakers should be covered with split watch glasses to exclude foreign material and prevent loss of solution through evolution of spray.

Electrodes

Platinum electrodes are most satisfactory for the general run of work. Different forms are used, including dishes and crucibles for cathodes. For stationary electrodes a gauze cathode and a spiral wire anode are very satisfactory. Foil cathodes may be used, but usually the rate of deposition must be kept lower than with the gauze form, in order for the deposit to adhere well.

Various other materials have been tried for electrodes. Tantalum has been used for a few metals, especially copper. A solution of trichloro-

[9] See Elving, Hayes, and Mellon, *J. Chem. Educ.* **30**, 254 (1953).

acetic acid, containing a little ammonium trichloroacetate, serves to remove the copper deposit. Even then it is difficult in student use to keep the surface of the electrode sufficiently free of oxide to obtain satisfactory deposits.

Copper-gauze electrodes may be used for the deposition of copper in instructional laboratories. Such electrodes can be made by the students from wire gauze.

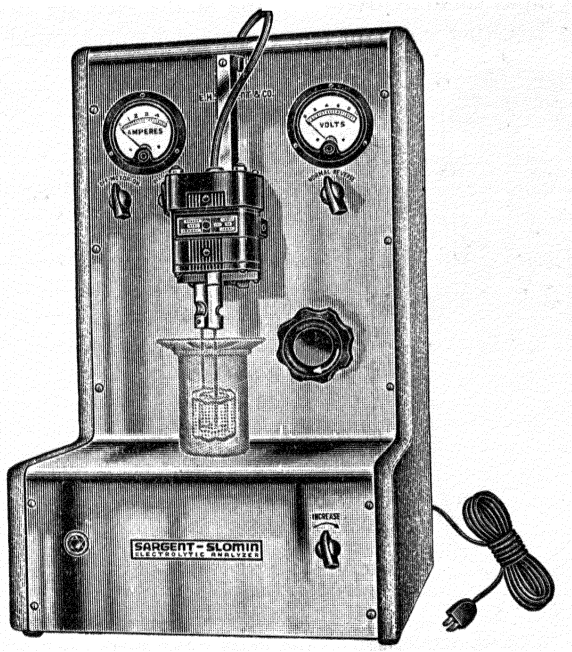


Figure 9.4

View of a commercial apparatus for electrodeposition (courtesy E. H. Sargent and Co.).

The use of mercury as a cathode is advantageous in some cases where platinum is not satisfactory.[10] There are two general cases: (1) the solution is "cleaned up" by depositing the interfering elements in the mercury, as in the determination of uranium;[11] and (2) the desired constituent, such as an alkali metal, is deposited in the mercury. In the latter instance, following replacement of the electrolyte by water,

[10] For a discussion of the mercury cathode and its applications, see Maxwell and Graham, *Chem. Rev.* **46**, 471 (1950).

[11] In general, metals below manganese in the emf series can be made to deposit quantitatively in a mercury cathode. See Rodden *et al., Analytical Chemistry of the Manhattan Project,* p. 511, McGraw-Hill, 1950.

the alkali metal is measured titrimetrically. Overvoltage effects are very important here.

Vessels for a mercury cathode must have a special form. One of them is illustrated in Figure 9.5. This is the Melaven type, as recommended by the ASTM. A complete mercury cathode apparatus is illustrated in Figure 9.6. In this "Dyna-Cath" apparatus, the electrolyte and mercury become two independent rotors of a direct-current motor and create rapid countercurrent stirring at the mercury-electrolyte surface. The resulting clean mercury surface assures rapid electrolysis.

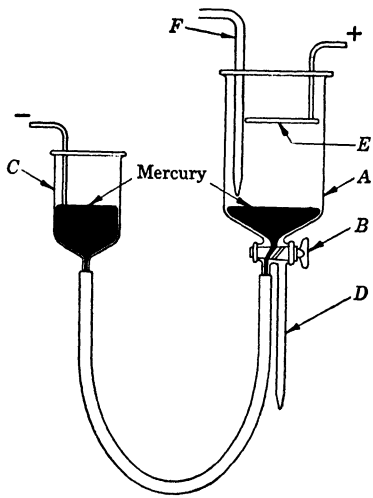


Figure 9.5

Melaven type of mercury cathode cell. *A*, cylindrical glass vessel with conical base; *B*, two-way stopcock; *C*, leveling bulb; *D*, glass tubing constricted in same manner as a buret tip; *E*, platinum gauze or coiled platinum wire; *F*, narrow glass tube for introduction of air to stir the electrolyte (a motor-driven stirrer can be used instead) (reproduced with permission of American Society for Testing Materials).

For high rates of deposition, some cells have water jackets to provide for cooling the system.

Various types of stirring devices have been used for the electrolyte. The main objective of stirring is to decrease the time of deposition, since it permits use of a higher current. Rotation of one of the electrodes, usually the anode, is most common. For speeds of 300 to 400 r.p.m. a special form of anode is necessary. Many depositions of copper, for example, can be made under these conditions in 15 to 20 min. instead of the 2 to 3 hours necessary with stationary electrodes. An air stream is used in the author's apparatus.

FACTORS AFFECTING THE NATURE OF THE DEPOSIT

From the standpoint of the analyst an electrolytic deposit, such as copper, in addition to being quantitative should be pure and should

adhere well to the electrode. Various factors influence the nature of deposits, and they may be impure, spongy, discolored, or nonadherent.

Some elements are deposited in good condition more readily than others. Thus, copper deposits well from a nitrate solution, but silver gives crystals which do not adhere well.

Silver deposits best from a solution of the complex cyanide ion $Ag(CN)_2^-$. In contrast, lead deposits best on the anode as the dioxide from a solution containing some 10 per cent of nitric acid and a few drops of hydrogen peroxide. Some elements tend to be spongy if much hydrogen is evolved at the cathode during deposition.

In some cases a temperature of 60 to 70° is recommended. In other cases this temperature seems to foster spongy deposits.

Some deposits can stand a much higher amperage than others. For copper it is usually advisable to start at 0.1 amp. with stationary electrodes. If the deposit is satisfactory after a few minutes, the rate may be increased gradually as long as the appearance remains good. In any case, too rapid deposition gives nonadherent deposits.

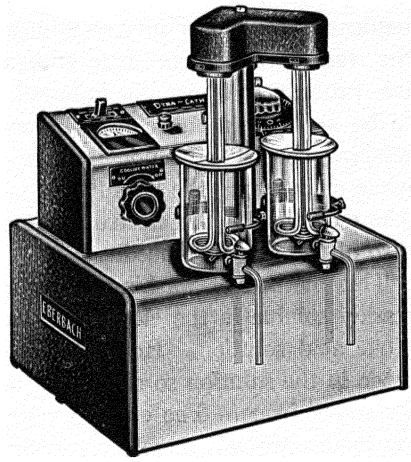


Figure 9.6

Mercury cathode apparatus (courtesy Eberbach & Son Company).

In contrast to copper, nickel may be started at 1 amp. from an ammoniacal complex solution, and iron from an oxalate complex at 1 to 2 amp.

Currents that cannot be tolerated with stationary electrodes give good results with rotating electrodes. A motor-driven stirrer or a stream of air bubbled through the solution provide stirring when stationary electrodes are used.

A large and roughened surface usually promotes adherence of the deposit. A sand-blasted electrode (as found in the Classen dish), or a gauze electrode is preferable to a smooth foil electrode.

Disposal of the Products

Following separation of one or more constituents of a solution on the electrodes, different methods for continuing the analysis may be followed.

Two of the most likely may be noted: (1) The deposit on the electrode may be weighed, as in the determination of copper. (2) The deposit, the solution, or both, may be used in effecting further separation and/or measurement. Impurities in the uranium used in atomic energy processes can be separated from the uranium itself by electrolysis into a mercury cathode. The mercury may then be volatilized. The residue of impurities left is dissolved and the individual components therein determined by suitable technics.

In handling a deposit such as copper on a platinum electrode, the first problem is to wash it thoroughly. Unless the deposit has no tendency to go back into solution on breaking of the electrical circuit, the washing should be done without interrupting the current. One of two procedures is usually followed. If the electrolyzed solution is not to be kept for a subsequent operation, a very satisfactory method of washing consists in siphoning the solution out of the electrolysis cell while maintaining the liquid level in the vessel by adding distilled water. The depletion of the electrolyte is shown by the dropping back toward zero of the ammeter needle.

This method of washing is particularly suitable when the deposit is readily soluble in the electrolyte, as in the deposition of copper from a nitric acid solution. However, if a subsequent determination is to be made in the solution so obtained, this method involves too much volume for convenience. The usual practice of washing then consists in lowering the electrolysis vessel slowly while washing the deposit with a stream of water from a wash bottle.

In either method of washing, completion of the process means reducing the current practically to zero. When two determinations are running in series, as provided for in the apparatus illustrated in Figure 9.2, the deposit in the cell not being subjected to washing may start to dissolve when the current ceases to flow (this will happen with copper being deposited from nitric acid solution). Obviously, on completion of the washing of the first cell, the second cell should be allowed to electrolyze a little longer, so that any dissolved metal may be redeposited.

Deposits that are easily oxidized when wet, such as iron, may be rinsed with ethanol to remove water before being dried in an oven, as a preliminary to weighing. In the occasional case where a deposit in a mercury cathode is weighed, the mercury is washed (in the vessel) with water, ethanol, and diethyl ether, in that order.

Metallic deposits are generally dried at 105 to 110°. In the case of lead dioxide there has been much argument, some investigators maintaining that it must be dried at 230° in order for all the water to be removed

and for the theoretical factor (Pb/PbO_2) to apply. Amalgams secured by use of the mercury cathode, if weighed, are air-dried following the washing with ethanol and diethyl ether.

After weighing deposits such as copper or nickel, they are removed from the electrode by means of a suitable solvent. If a few cases, such as nickel, the electrode must be inspected carefully, as the deposit resembles platinum closely and does not dissolve quickly.

The usual practice consists in weighing the electrode before and after deposition to obtain the weight of the deposit. In some cases there is evidence that a small transfer of platinum takes place during electrolysis. If so, the deposit should be weighed, dissolved, the electrode alone weighed, and the difference taken as the weight of the deposit.

APPLICATIONS OF ELECTRODEPOSITION

In general, electrodeposition serves two purposes: (1) the separation from a solution of components that otherwise would interfere with the determination of a desired constituent; and (2) the separation of the constituents to be determined.

Utilization of this technic for the first purpose is exemplified best by the removal of various metals that would prevent the determination of uranium, as mentioned under the description of the mercury cathode cell.[12]

Use of electrodeposition as part of the procedure for the determination of elements is largely limited to those elements that can be deposited and handled quantitatively. The measurement is usually gravimetric, although a titrimetric method may be used, as with the alkali metals.

Some 25 to 30 metals can be separated readily as the elements themselves, and a few as the oxides. Of the nonmetals, chlorine and bromine in limited amounts may be deposited on a silver-plated or silver electrode.

Certain compounds may be determined. Thus, a solution of sodium chloride can be electrolyzed in a Hildebrand cell, with a mercury cathode and a silver-plated anode. The chlorine, combined with the silver on the anode, is weighed directly. At the end of the electrolysis, when any remaining solution is siphoned out and replaced with water, the current is reversed. This causes the amalgam to decompose rapidly, with the formation of an amount of hydroxyl ion equivalent to the sodium. Titration may then be made with an acid.

In addition to the separations that are possible when elements are in solution singly, the analyst is concerned with the possibility of separation

[12] Rodden *et al., loc. cit.*

in solutions in which two or more elements occur together. Following are three general types of elements that fall into this second category.

1. Those which cannot be separated from aqueous solution on platinum electrodes. This group includes the alkali and alkaline earth metals.

2. Those deposited, under suitable conditions, on the anode as oxides. This group is small, including, generally, lead (PbO_2), manganese (MnO_2), and thallium (Tl_2O_3).

3. Those deposited on the cathode. Each in this group is deposited as the metal, with the exceptions of molybdenum and uranium, which form oxides (Mo_2O_3 and U_3O_8).

These three groups may be separated easily, the emf having little significance as long as deposition continues. Perhaps the most important problem involves separation of various elements included in the third group. The two general procedures for this separation involve control of the potential applied and of the composition of the solution.

The graded potential method is based upon proper adjustment of the applied voltage. This is the usual type of electrodeposition separation. The voltage is controlled manually to prevent deposition of undesired elements with decomposition potentials above that of the desired element. Thus, if any two elements to be separated have standard electrode potentials at least 0.2 volts apart, the voltage may be set and maintained between the two decomposition potentials. After the element of lower decomposition potential has been deposited, the voltage may be increased enough to effect deposition of the other element.

Such separations may be refined by the use of the controlled cathode potential technic. In this variation, the applied voltage is kept at the minimum value necessary to effect the desired separation. Control is maintained through measurement of the potential difference between the cathode at which deposition is taking place and a suitable reference electrode, such as a calomel cell (see Chapter 18). The applied voltage can be controlled automatically by suitable instrumentation.[13]

Another approach is to vary the composition of the solution in order to control the electrode potentials of the elements present. For example, the *p*H may be changed or complexing agents may be added to shift standard electrode potentials. In acidic solution, copper ($E^0 = -0.34$ volts) and cadmium ($E^0 = +0.40$ volts) can be readily separated, the copper depositing first. In cyanide solution both elements form complex ions. Here cadmium can be separated first because of its greater ease of electroreduction in this environment. The tetracyanocadmiate

[13] Caldwell, Parker, and Diehl, *Ind. Eng. Chem., Anal. Ed.* 16, 532 (1944); Lingane, *Ind. Eng. Chem., Anal. Ed.* 17, 332, 640 (1945), and *Electroanalytical Chemistry*, Wiley, 1954.

ion $Cd(CN)_4^{-2}$ is much more dissociated than is the tricyanocuprate ion $Cu(CN)_3^{-2}$.

As advantages of electrodeposition methods, the following may be noted: (1) the process requires little attention after the electrolysis is started; (2) the rate is easily controlled, thus making overnight separations practical; (3) many of the depositions can be completed rapidly, if necessary; (4) the deposit does not require any extended washing or ignition; (5) the purity of the deposit is usually acceptable; and (6) for a few elements, such as copper and cobalt, the method is one of the best available.

The most obvious disadvantages are as follows: (1) commercial apparatus, including batteries and electrodes, is somewhat expensive, especially for large student classes; (2) some separations of one metal from another are relatively slow, especially when their electrode potentials are so close together that it is impossible to set the voltage far above the lower of the two; and (3) the method is limited to certain elements, primarily the metals.

Displacement Separations

A few important electrochemical separations, based upon the use of the relation of the chemical elements in the emf series, do not involve the application of an external potential to the solution. This type of electrolytic separation is usually called *displacement*. A qualitative example is the old trick of copper-plating an iron wire nail by dipping it into a solution of cupric sulfate. The iron displaces the copper, which then adheres to the nail.

In the determination of copper in an ore, for instance, a piece of aluminum foil may be placed in the acidic solution containing the cupric ions, whereupon the copper is deposited as such on the aluminum (Exercise 28.9). The deposit may then be dissolved and its amount suitably measured. A similar method may be followed in the analysis of a zinc ore (Exercise 27.6). In this case, the separation is made to remove interfering elements below aluminum in the emf series.

Efficiency of Separation

Assuming the applicability of standard electrode potentials, one may calculate the point of equilibrium for such a separation by use of the Nernst equation. When aluminum is used to displace copper, some of the aluminum goes into solution and an equivalent amount of copper deposits, the reaction proceeding according to the equation

$$2\ Al + 3\ Cu^{+2} \rightarrow 2\ Al^{+3} + 3\ Cu$$

Applying the principle of equilibrium, we have,

$$\frac{[Al^{+3}]^2 \times [Cu]^3}{[Al]^2 \times [Cu^{+2}]^3} = K$$

On elimination of the terms $[Cu]^3$ and $[Al]^2$, which represent concentrations of metals in the solid form and, therefore, constant activities. the equation becomes

$$\frac{[Al^{+3}]^2}{[Cu^{+2}]^3} = K$$

indicating that the reaction will reach equilibrium when the concentration of aluminum ions bears a given ratio to that of the copper ions. By means of standard electrode potentials and the Nernst equation, the value of K may be calculated.

For the aluminum electrode, we have

$$E_{Al} = E^0_{Al} - \frac{0.0591}{3} \log [Al^{+3}]$$

and for the copper electrode

$$E_{Cu} = E^0_{Cu} - \frac{0.0591}{2} \log [Cu^{+2}]$$

At equilibrium the electrode potential of the aluminum will equal that of the copper. Therefore,

$$E^0_{Al} - \frac{0.0591}{6} \log [Al^{+3}]^2 = E^0_{Cu} - \frac{0.0591}{6} \log [Cu^{+2}]^3$$

On substituting the values of $+1.7$ for E^0 for aluminum, and of -0.34 for E^0 for copper, and calculating the equilibrium constant, we obtain a value (K = approximately 10^{200}) which seems absurdly large. Presumably this is the result of a lack of accurate knowledge concerning the electrode potential of aluminum and the activities of the aluminum and copper ions.

Internal Electrolysis

In some cases, such as the displacement of copper with aluminum, simple immersion of the displacing metal is sufficient. An interesting variation of this kind of separation was proposed by Clarke, Wooten, and Luke,[14] and called internal electrolysis. The process involves the spontaneous discharge of a galvanic cell in which the solution to be analyzed is made the catholyte or anolyte liquid into which a rotating

[14] *Ind. Eng. Chem., Anal. Ed.* 8, 411 (1936). See also Lingane, *Electroanalytical Chemistry*, p. 333, Wiley, 1954.

electrode dips. The displacing metal is placed in an alundum thimble which dips into the sample solution. Then the displacing metal electrode is simply connected to the platinum electrode dipping into the sample solution. This arrangement provides a rapid, inexpensive automatic control of the cathode potential.

Internal electrolysis has been used chiefly for the separation of minor impurities in metals. Thus, minute amounts of bismuth and copper can be determined in nearly pure lead by dissolving a sample and using a piece of lead as the dissolving electrode. The American Society for Testing Materials recommends specific apparatus for such purposes.[15]

[15] *1950 Book of ASTM Methods for Chemical Analysis of Metals*, Amer. Soc. Testing Materials, p 17.

CHAPTER 10

SEPARATION BY PARTITION PROCESSES

In the discussion of methods of separation in the preceding chapters, several kinds of selective action of reagents were mentioned. Still other principles of selective action of different reagents toward the components of a sample are used extensively. These methods, too, enable the analyst to isolate from the sample either the desired or the interfering constituent(s). Through the successive application of different reagents it is possible often to remove several constituents, one after the other.

Whenever such a procedure is practical, the sample is treated directly with the reagent. Sometimes, however, certain preliminary chemical transformations of the sample constituents are necessary, in order that products having the desired chemical properties, such as solubility relationships, may be secured.

To designate all the different kinds of processes considered in this chapter the term "partition" has been adopted. The term "extraction" has been used in this broad sense by some writers; more often, however, it has been used to include only selective dissolution and/or liquid-liquid transfer processes.

In partition methods of separation a phase P_1 containing the desired constituent is brought into contact with a second phase P_2 in which the desired (or interfering) constituent is more "soluble" than in P_1. At the place of contact of the two phases, competition occurs between them for one of the constituents, which is consequently transferred to a greater or lesser extent to the second phase. The final operation involves mechanical separation of the two phases. By the placing of fresh portions of phase P_2 successively in contact with phase P_1, which is being depleted in the desired (interfering) constituent, phase P_1 is eventually totally depleted of the constituent being transferred. For example, a solid mixture of sucrose and sand may be brought into con-

tact with water. The sucrose dissolves in the water and leaves the sand behind. Here, P_1 is the original solid phase and P_2 is the liquid phase introduced.

The transfer of a constituent from one phase to another may be largely physical in nature, or it may involve chemical reaction with the new phase, P_2. In a great number of cases of this general type of separation, the mechanism involved seems to be dissolution or some kind of compound formation.

Processes based upon phase competition include all of the so-called extraction, distribution, and partition methods. This type of process ultimately involves equilibration between phases and the equilibrium distribution of the desired constituent between the two phases. Table 10.1

TABLE 10.1

SEPARATION PROCESSES BASED ON TRANSFER BETWEEN PHASES

Phases in Contact		*Typical Separation*	
Original	Added	*Technic*	*Example*
Gas	Gas	De-gassing	Removal of dissolved gases
Gas	Liquid	Absorption	Orsat gas analysis
Gas	Solid	Adsorption	Turner-Burrell apparatus
Liquid	Gas	Evaporation	Drying in an air stream
Liquid	Liquid	Extraction	Organic separations
Liquid	Solid	Adsorption	Columnar processes
Solid	Gas	Evaporation	Drying in an air stream
Solid	Liquid	Dissolution	Soxhlet apparatus
Solid	Solid	Solid solution	Carrier action

lists various types of partition processes, as well as certain others which involve the transfer of a constituent from one phase to another.

It may be noted that these partition processes are distinguished by the *transfer* of a constituent *from* one phase to another. From the standpoint of phase relations, the three main processes of separation previously discussed are distinguished by the *formation* of a phase which then separates.

The literature relating to the processes grouped in this chapter is still in a relatively unorganized state. The nature of the processes is somewhat diverse. Many facts concerning them are recorded in various places, and extensive application has been made of some of the processes for a long time. Much work is still too recent to have been given proper trial and acceptance. In part, the lack of systematic presentation of these technics as separative processes is attributable to failure to look

upon them as distinct from the measuring operations of general methods of analysis.

In view of this situation, the material in this brief consideration of partition processes is subdivided on the basis of the physical states of the samples to be treated and the reactants employed. The nature of the process, the means employed, the nature and disposal of the products, and the applications of the methods are treated together in each subdivision.

ACTION OF A SOLID WITH A LIQUID

There are two viewpoints from which to consider the separative reactivity of solids and liquids with each other. One is concerned with a determination of which phase originally contains the desired constituent and which phase is the reacting medium. These two possibilities are discussed separately as dissolution and adsorption processes.

Dissolution Methods

If the solid phase contains the desired constituent and the reactive phase is a liquid, the separative process may be designated as selective dissolution.[1] The product of the process is a solution.

In this kind of separation, part of a sample is *transferred from* the solid to the liquid phase. In contrast, in precipitation, discussed in Chapter 8, part of a sample is *converted into* a solid phase.

Selective dissolution methods depend upon pronounced differences in solubility, in a suitable medium, of various parts of the sample system. Usually the separation is made by dissolving the desired constituent in some liquid in which the solubility of any other substances present is so small as to be negligible. Sometimes the process is just the reverse, in which case the desired constituent is insoluble and all else goes into solution.

The process of dissolution may be of two types. In one type the action is often spoken of as being largely physical in nature, since it involves a minimum of chemical interaction between the sample components and the added solution constituents. An example is the dissolution of sodium chloride in water. Of course, in many cases, if not all, the dissolution is accompanied by hydration (solvation) of the dissolved substance or its ions. The solvent in these cases is often said to be inert; actually, the process of solvation may be considered chemical in nature.

[1] This process has often been called extraction and the equipment used extractors. In this book extraction refers to liquid-liquid processes.

In the second type, a chemically active solvent is employed. In this case, dissolution results from an ordinary chemical reaction to form a soluble product; for example, lime (calcium oxide) dissolves readily in hydrochloric acid to form soluble calcium chloride. The solvent employed in this second type often contains an acid, a base, or a compound capable of forming soluble complex ions.

Since dissolution is often only the reverse of precipitation, some of the factors and laws underlying precipitation apply also to dissolution

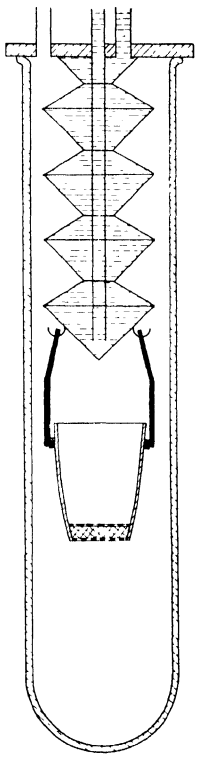
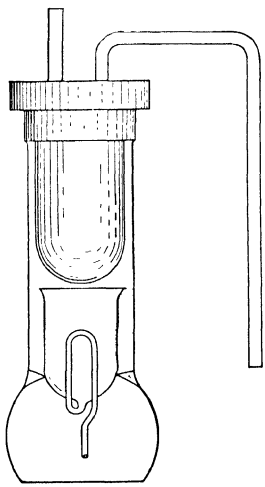


Figure 10.1 (left)

Wiley leaching apparatus.

Figure 10.2 (below)

Unit of a Bailey-Walker leaching apparatus.



processes. Accordingly, such equilibrium processes as complex formation, ionic dissociation, and reaction of solvents must be taken into account.

The theory of dissolution takes no account of the time required for the action to take place. In practice, dissolution may require several hours. In order to avoid the use of large quantities of solvent, analysts have devised types of leaching (extraction) apparatus. Most of these

devices are used in the removal of organic matter, such as fats, from various raw products. Others are used for the dissolution of active principles from crude drugs.

These leaching devices (extractors) may be classed as continuous or intermittent. The continuous type, exemplified by the simple Wiley apparatus, is illustrated in Figure 10.1. The solvent, placed in the outside container, is boiled and the vapor rises around the crucible to a metal condenser, where it is condensed and falls back on the solid to be selectively dissolved. The solvent then leaches through the solid and the porous bottom of the crucible back into the original flask.

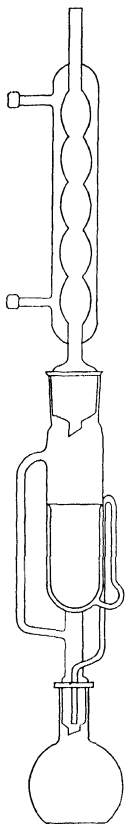


Figure 10.3
Soxhlet leaching apparatus with paper thimble.

The Bailey-Walker leaching apparatus illustrates an intermittent type. In it the solvent is also boiled and allowed to come into contact with a metal condenser from which the liquid falls back on the sample contained in a small cup fitted with a siphon, as shown in Figure 10.2. When the solvent collects in the cup to a sufficient height, the liquid siphons out into the container below. The process may be repeated until dissolution of the required constituent is complete.

Figure 10.3 illustrates the well-known Soxhlet assembly fitted with glass joints. In the type illustrated the operation is intermittent, as with the Bailey-Walker type. Soxhlet equipment is also made without the side siphon, and is open so that the condensed liquid may fall back on the sample and then go on through to the flask below.

Samples to be leached by a liquid are handled in various ways. Solids are generally placed directly in a paper or alundum thimble in apparatus such as the Soxhlet type. In the Wiley type they are put in the crucible. Liquid samples, such as milk, may be absorbed in a specially prepared paper which is then placed in the apparatus. Often the sample is simply placed in contact with the solvent in an open vessel that may be heated. In such cases, stirring may aid in accelerating the rate of dissolution of the soluble material.

The following are familiar examples of separations accomplished in this manner: the dissolution of fats in foodstuffs by means of diethyl ether; the dissolution of everything except the gangue in ores by means

of acids, and the determination of potassium, which involves a conversion of sodium and potassium to the perchlorates and a leaching of the sodium salt with a mixture of equal volumes of *n*-butyl alcohol and ethyl acetate.

The analyst must know, or determine, that the desired separation can be accomplished with a given reactant under the operative conditions to be maintained. For example, a constituent readily soluble by itself in a given solvent may not so react in association with other constituents. This fact seems to be generally true of metals in alloys. Consequently, in the analysis of alloys one rarely separates one metal after the other by selective dissolution.[2]

Adsorption Methods

If a liquid phase contains the desired constituent and the reactive phase is a solid, the separative process may be one of several types. When there is no exchange of matter between solid and liquid, the separative process may be called *adsorption.* Reference was made in Chapter 8 to this ability of certain solids to condense on their surfaces, or adsorb, different substances from a solution surrounding the solid particles.

The process of adsorption is then a kind of immobilization of part of the sample solution *on* a solid in contact with the solution. A long-known example of adsorption in water analysis consists in collecting very small amounts of lead ions by shaking the sample with solid calcium carbonate. The centrifuged, unwashed solid is then dissolved in acetic acid and the lead precipitated as the chromate. A preparative, non-analytical example is the filtration of a colored solution of sucrose through a bed of adsorbent, such as specially treated carbon, to decolorize the solution before crystallization of the sugar.

Both of these examples may be considered as types of general adsorption, that is, a more or less complete removal of the adsorbed constituent(s) on the adsorbent is effected. The solid may be simply shaken with the solution in a beaker, after which the two phases are separated by filtration and washing; or the solution may be poured down through a tube packed with the adsorbent. A nonquantitative example of this type, mentioned in Chapter 8, is the adsorption of ferric ion during the precipitation of barium sulfate.

The same type of general adsorption is found in the action of "carriers" or gathering agents.[3] In this case, a fairly large amount of precipitate

[2] This should be kept in mind if the library assignment in Chapter 32 is a polycomponent alloy.

[3] Willard and Diehl, *Advanced Quantitative Analysis,* p. 38, Van Nostrand, 1943.

carries with it practically all of a minor constituent. For example, in the ASTM method for determination of arsenic and antimony in brass (Exercise 31.3 *b*) iron added to the sample solution is precipitated with ammonia. The large amount of hydrous ferric oxide so formed carries with it the arsenic and antimony, which may then be filtered off, dissolved, and determined.

In contrast to general adsorption, we may distinguish a *differential* or *fractional* type. In this type, two or more dissolved substances, often closely related chemically, are selectively held by the adsorbent. Thus, they are separated not only from the solution but also from each other by being adsorbed at different positions on the solid. A striking example of differential adsorption is the separation of two very closely related chlorophylls, dissolved in hexane, by pouring the solution down through a column packed with finely divided particles of sucrose. One of the two chlorophylls is adsorbed nearer the top of the adsorbent column than the other. In this case, the separation of the two compounds is readily apparent, as they have different colors.

This differential process has come to be designated by many as *chromatographic adsorption,* the chief reason being that one of the earliest examples of the process resulted in constituents of different hues. Today the expression "chromatography" and its related term "chromatographic" seem unfortunate. Often there is no distinguishing hue (color), although the prefix *chroma-* implies color. Then, too, the suffix *-graph* is questionable. "Columnar" or "differential" adsorption seem to be preferable terms.

With the use of a column to hold the adsorbent, this type of separation follows essentially the following steps:

1. A column of adsorbent, such as alumina or silica gel, is suitably prepared and packed in a vertical glass tube.

2. The solution containing the substances to be separated is poured into the top of the tube. The solution percolates down over the adsorbent particles and adsorbable solutes are adsorbed on the solid.

3. A developing liquid is poured into the tube. The passage of this liquid or solution down the tube helps to separate the adsorbed substances along the length of the column. The most lightly adsorbed substances are carried toward the bottom of the column, while the more strongly adsorbed substances remain near the top.

4. The adsorbed substances can be removed for measurement or for further manipulation in one of two ways: (*a*) A suitable desorbing solvent may be poured through the tube. This results in the elution or removal of the substances, with the less strongly held substances coming

out of the tube first. (*b*) The whole column of adsorbent may be removed from the tube and cut into sections, each of which holds a substance or group of substances. This is followed by dissolution with suitable solvents of the adsorbed materials.

One type of simple adsorption apparatus is illustrated in Figure 10.4; many variations have been proposed for different situations.

Adsorption separations are illustrations of the fact that a process may serve primarily either preparative or analytical ends. The technic came into general use largely for preparative purposes, and for decades it has been found increasingly useful. A good illustration of successive, general adsorption was reported by Rosenberg,[4] who separated a complicated mixture into fractions by the use of selective adsorbents. He first adsorbed the carboxylic acids from the mixture by shaking the solution with talcum. Next, albumin was adsorbed on kaolin. This was followed by the use of moist hydrous ferric oxide to adsorb starch. The amino acids, carbohydrates, and peptone were left in the filtrate. The remaining problem of separating each of the constituents in the polycomponent fractions for analytical measurement will indicate something of the formidable difficulties encountered in biochemistry.

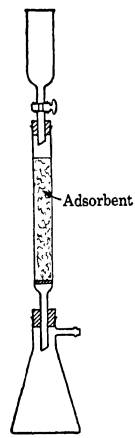


Figure 10.4

Column packed for adsorption separation.

The major developments of adsorption separation in preparative chemistry have been in the fields of biological and organic chemistry. The subject has been summarized in several books.[5]

From the viewpoint of the analyst, Strain's reviews[6] are very helpful for understanding recent work.

The selective removal of constituents in a packed column may be considered as fractional adsorption *on* the adsorbent. The reverse process, successive removal of constituents *from* the adsorbent, is called "desorption." Usually desorption is accomplished by allowing suitable liquids or solutions to percolate down through the column of adsorbent.

[4] *Kolloid-Z.* **37,** 234 (1925).

[5] Berl, "Physical Methods of Chemical Analysis," in *Chromatographic Analysis,* Vol. II, pp. 591-617, Academic, 1951; Bolston and Talbot, *A Guide to Filter Paper and Cellulose Chromatography,* Reeve Angel, 1952; Cassidy, *Adsorption and Chromatography,* Interscience, 1951; Pollard and McOmie, *Chromatographic Methods of Inorganic Analysis,* Academic, 1953; Smith, *Inorganic Chromatography,* Van Nostrand, 1953; Strain, *Chromatographic Adsorption Analysis,* Interscience, 1942; Weissberger, ed., *Techniques of Organic Chemistry,* Vol. V, *Adsorption and Chromatography,* Interscience, 1951; Zechmeister and Cholnoky, *Principles and Practice of Chromatography,* Chapman and Hall, 1941.

[6] *Anal. Chem.* **21,** 75 (1949); **22,** 41 (1950); **23,** 25 (1951); **24,** 50 (1952); **25,** 90 (1953).

A different kind of desorption technic is illustrated in an apparatus for the automatic separation of low-boiling compounds by fractional desorption.[7] In this apparatus the sample of gases, ranging in boiling point from hydrogen to C_5-hydrocarbons, is adsorbed on a long column of charcoal. Along its length the compounds arrange themselves approximately in the order of boiling point, the lowest-boiling components being uppermost in the column. Hot mercury is then passed up the column to sweep out the gas column before it. As each gas leaves the column, it passes through a thermal conductivity cell in which measurement serves to identify the gas. The volume of the gas is then measured by a device in which the gas pushes a small slug of mercury around a standard path, the number of times the slug passes an electromagnetic field in the path being automatically counted and recorded.

The record obtained is analogous to that for analytical distillations. Whereas the low-temperature Podbielniak distillation apparatus plots pressure (quantitative measure) against temperature (qualitative indication) the Turner-Burrell apparatus records volume in terms of number of circuit-paths traversed (quantitative axis) against thermal conductivity (qualitative axis). Since thermal conductivity does not necessarily increase with boiling point, the curve often has sharper "breaks," and minor components are more readily detected, than in fractional distillation.

An interesting variation in adsorption separations involves the use of paper of suitable grades as the solid adsorbent. Many analysts refer to this technic as *paper chromatography*. In applying the process, the liquid solution containing the solutes to be separated is allowed to pass by capillary action into the paper. The paper may be impregnated with some reagent to bring about a desired reaction, such as color formation, with particular constituents. An interesting application of this technic to twelve of the amino acids has been described by Bull, Hahn, and Baptist.[8] Clegg[9] has summarized analytical possibilities to date.

Ion-Exchange Methods

A technic that resembles, at least superficially, separations by adsorbent action is known as ion exchange. Analysts agree that in true adsorption the adsorbate is merely condensed on the surface of the

[7] The Turner-Burrell adsorption fractionator, the Burrell Technical Supply Co., Pittsburgh, Pa.

[8] *J. Am. Chem. Soc.* **71**, 550 (1949).

[9] *Anal. Chem.* **22**, 48 (1950).

adsorbent, that is, that there is no interchange of any specific part of the adsorbent with the solution brought into contact with the solid.

In contrast, ion-exchange methods are based on the removal of cations and anions from solution by replacement with other ions or by chemical combination.

The agents currently in use for effecting ion exchange are mostly organic compounds of high molecular weight, known as "resins." These compounds usually remove cations by a base-exchange process in which the cations are replaced by sodium ion or hydrogen ion. Anions are usually removed by prior conversion to the corresponding acid. The latter is then removed by combination with a basic resin. These removal processes are illustrated by the following equations in which R represents part of a resin molecule:

$$Ca(NO_3)_2 + 2\,HR \rightarrow 2\,HNO_3 + CaR_2$$
$$NaCl + HR \rightarrow HCl + NaR$$
$$HCl + RNH_2 \rightarrow RNH_3Cl$$

The extensive development and utilization of ion-exchange technics are fully described in the literature.[10] Recent reviews indicate the current interest in these technics.[11] It may be noted that resins are now being tailored to do specific jobs in preferential separation, that is, one resin may remove anions of strong acids, and another may remove anions of weak acids.

The application of ion exchange to analytical chemistry includes (1) isolation of desired constituents on columns of ion exchangers from which the constituents can then be removed in solution, (2) removal of interfering substances, and (3) separation of mixtures by a technic similar to that described for differential adsorption.

Perhaps the most striking recent development is the separation of the rare-earth elements.[12] The laboratory process has been adapted to industrial separation.[13]

ACTION OF A LIQUID WITH A LIQUID

One of the older partition methods is often referred to as a liquid-liquid extraction process. The author limits the use of the word "extraction" to this technic. Although long known, the process has not enjoyed wide use until recently.

[10] Nachod, *Ion-Exchange Theory and Practice*, Academic, 1949; Samuelson, *Ion Exchangers in Analytical Chemistry*, Wiley, 1953.

[11] Kunin, *Anal. Chem.* **21**, 87 (1949); **22**, 64 (1950); **23**, 45 (1951); **24**, 64 (1952); **25**, 104 (1953).

[12] Series of papers, *J. Am. Chem. Soc.* **69**, 2769-2881 (1947).

[13] *Chem. Eng. News* **29**, 3015 (1951).

In this process, advantage is taken of the difference in solubility of the desired constituent in two immiscible liquid phases. When such liquids are in contact, any solute originally present in either of them distributes or divides itself between them in a ratio that depends upon the ratio of the solubilities of the solute in the two liquids, and upon the solubility of the two liquids in each other. If the two liquids have a very slight mutual solubility, and if the solute has a very much greater solubility in one liquid than in the other, one liquid will contain a very large percentage of the solute at equilibrium. This phase may then be separated mechanically by means of a separatory funnel. By repeated treatments in which the original liquid solution is brought into contact with fresh portions of the second liquid, the desired constituent can be removed as completely as desired.

The distribution of some solute, such as iodine, between two immiscible solvents, such as carbon tetrachloride and water, takes place according to Henry's law.

$$\frac{[I_2]_{(CCl_4)}}{[I_2]_{(H_2O)}} = K$$

that is, the *ratio of the concentrations (activities) in the two solvents is a constant for a given temperature.* The constant, K, is known as the "distribution coefficient." For the iodine system being considered, the value of K is about 85 at room temperature. Therefore, when the system is in equilibrium, the carbon tetrachloride layer contains 85 times as much iodine per unit volume as the water layer. The actual amount of iodine in each solvent will be the product of the volume and the concentration.

Liquid-liquid extraction has long been practiced in the separation of organic compounds, both in the laboratory and in industrial plants. To a lesser degree this method has been adapted to analytical purposes. The use of the process for separating inorganic constituents has long been known, but it has been much less extensively used. A few methods, such as the Rothe separation for iron, have been of some importance.

The Rothe method is used for the separation of iron from certain other metallic constituents in 6 M hydrochloric acid by shaking the solution with diethyl ether saturated with hydrogen chloride. Under the proper conditions, 98 per cent of the iron will be found in the ethereal layer. Repeated extractions of the aqueous solution with fresh portions of ether will result in a quantitative separation. Although this use of diethyl ether is a classic example for liquid-liquid separation of iron, other solvents may also be used. Among these are di-isopropyl ether, β,β'-

dichlorodiethyl ether, amyl acetate, and acetylacetone.[14] New organic solvents suggest other possibilities.

Other examples of extraction of inorganic constituents into organic solvents, although not numerous, are not uncommon. Rodden[15] has reported what is probably the most intensive search for such methods. Figure 10.5 shows the apparatus developed for extracting uranium as uranyl nitrate.

Most progress in this direction has been made using organic compounds, usually those forming chelate-type complexes with metals, dissolved in an organic solvent. The organometallic complex is formed on shaking this reagent solution with the solution of the sample. As the complex is soluble in the organic liquid, it moves into this layer as formed. Dithizone (diphenylthiocarbazone) is a well-known reagent for such separations. Work with a large number of complexes of cupferron (ammonium nitrosophenylhydroxylamine) has been summarized.[16] Two examples of this kind of polycomponent samples are medicinals (As^{+5}, Bi^{+3}, Cd^{+2}, Cu^{+2}, Fe^{+3}, Ni^{+2}, Pb^{+2}, Zn^{+2}),[17] and industrial wastes (Cd^{+2}, Cr^{+3}, Cu^{+2}, Fe^{+3}, Mn^{+2}, Ni^{+2}, Pb^{+2}, Zn^{+2}).[18]

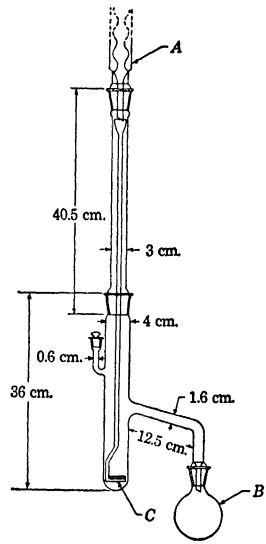


Figure 10.5

Extractor for uranium (reproduced with permission from C. J. Rodden, ed., *Analytical Chemistry of the Manhattan Project*).

The revived interest in inorganic separation by this method is exemplified by the fact that the first description of the preferential extraction of antimonic chloride over antimonous chloride by an ether was in 1911, but a workable analytical method was not published until 1949.[19]

The general area of extraction separations has been thoroughly discussed by Golumbic.[20]

[14] West, *Metallurgia* **43**, 41 (1951).
[15] Rodden *et al.*, *Analytical Chemistry of the Manhattan Project*, McGraw-Hill, 1950.
[16] Furman *et al.*, *Anal. Chem.* **21**, 1325 (1949).
[17] Strafford *et al.*, *Analyst* **70**, 232 (1945).
[18] Butts *et al.*, *Sewage Ind. Wastes* **22**, 1543 (1950).
[19] Edwards and Voight, *Anal. Chem.* **21**, 1204 (1949).
[20] Golumbic, *Anal. Chem.* **23**, 1210 (1951).

Fixed Solvent Modification

An interesting contemporary separative technic has been unfortunately named *partition chromatography*. As originally developed, this process was the first practical application of continuous countercurrent liquid-liquid extraction. It involves spreading the sample solution on a so-called inert absorbent that apparently holds the solution solvent fixed in place, thus forming an immobile liquid layer, or stationary phase.

The solution is then extracted with a second liquid phase, the mobile, or moving, phase. The latter extraction medium must have the following properties: (1) it must not be fixed by the adsorbent; (2) it must be immiscible with the stationary phase; and (3) it must be a better solvent for the solute constituents than the stationary phase. If the distribution coefficients of the solute species are sufficiently different, the eluate from the column will be a succession of pure solutions of the various solute compounds. Accordingly, the process is essentially countercurrent liquid-liquid extraction with one liquid phase fixed in position.

A solution of the C_1- to C_5-saturated fatty acids, which is very difficult to separate by other means, can readily be analyzed as a result of separation based on this technic. The acids are separated on a column of silica gel, saturated with an aqueous solution of brom cresol green indicator. The extraction solvent is 1 per cent butanol in chloroform. The indicator serves to show the position and movement of the acid bands in the column. Such a technic is particularly valuable for separations involving the whole molecule rather than for those involving position isomerism.[21]

ACTION OF A GAS WITH A SOLID

One of the methods used in gas analysis to separate a mixture of gaseous constituents is to bring the mixture into contact with a solid that has the desired selective action toward the constituents. One or more constituents will be removed by each such active solid. The nature of the process is likely to be one of the following types: (1) adsorption on the surface of the solid; or (2) chemical action with the solid to produce a liquid or a solid compound. In either case, knowing the volume of the gaseous mixture before and after the action with the solid enables the analyst to calculate the percentage by volume of the gas removed by each such reactant.

As examples of this type of separation, hydrogen may be adsorbed by finely divided palladium, and xenon may be adsorbed by suitably pre-

[21] See Craig, *Anal. Chem.* **22**, 1346 (1950).

pared charcoal. In some methods of gas analysis oxygen is separated from various other constituents by allowing the oxygen to react with solid yellow phosphorus. Carbon dioxide is often separated from air, or from oxygenated air (as in steel analysis) by absorption in soda lime or Ascarite. Water vapor, produced in burning of the hydrogen of organic compounds with oxygen, is absorbed in calcium chloride, calcium sulfate, phosphorus pentoxide, magnesium perchlorate, or other reactive solids.

ACTION OF A GAS WITH A LIQUID

Again, in gas analysis we find a number of examples of dissolution separations made by dissolving a gas in a liquid. Most gases display too little solubility in water to be separated by true solvent action. Separations may be readily effected, however, if the gas dissolves in a liquid through chemical action. An example is the dissolution of carbon dioxide in a solution of potassium hydroxide to form potassium hydrogen carbonate or potassium carbonate.

This type of process is common in gas analysis methods for separating one constituent of a gaseous mixture from other constituents. The mixture is bubbled through the absorbing reagent, which dissolves the gas to be determined. The main precautions in this process are that the reagent must be specific, and that there must be sufficient contact between the gas and the solvent. Examples of such separations are the absorption of carbon dioxide in a 35 per cent aqueous solution of potassium hydroxide, of ethylene in bromine water, and of oxygen in an alkaline pyrogallate solution.

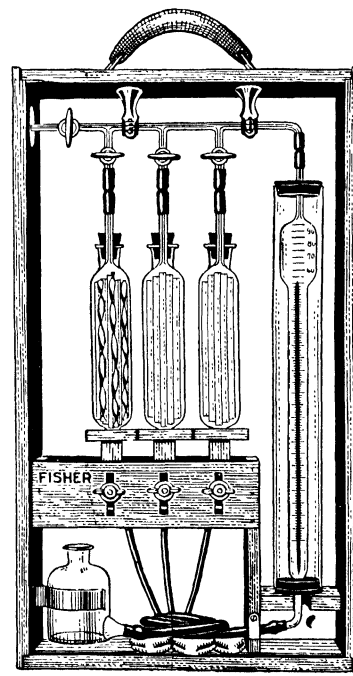


Figure 10.6

Orsat type of apparatus (courtesy Fisher Scientific Co.).

Many different types of apparatus for handling gases in this manner have been made. The type recommended by the U.S. Bureau of Mines is one of the best for precise work. Figure 10.6 illustrates one type of simple Orsat apparatus for making a

series of successive extractions on the same sample by specific reagents. It consists essentially of a row of vertical tubes (sometimes called "gas pipets") containing the absorbents, into which the gas can be passed, and a measuring buret for determining the volume before and after each reduction in volume by the absorbents.

ACTION OF A GAS WITH A GAS

Certain separations are made by dissolution of a gas in a gas, although ordinarily the desired constituent in the analysis is not involved. In removing hydrogen sulfide from a solution, for example, carbon dioxide may be bubbled through the solution, the result being a mixture or solution of hydrogen sulfide in carbon dioxide.

The efficacy of this method lies in the fact that in a bubble of pure carbon dioxide the partial pressure of the hydrogen sulfide is zero. If sufficient time and contact with the solution is then provided, the partial pressure of the hydrogen sulfide in the mixture of the gases will become equal to the hydrogen sulfide vapor pressure of the solution, and the hydrogen sulfide will be swept out of the carbon dioxide.

Another example of dissolution of a gas with a gas is the bubbling of carbon dioxide-free air through distilled water to sweep carbon dioxide out of the water.

APPLICATIONS OF THE METHOD

From the preceding discussion it is evident that partition methods of separation may have many and various applications. The extent to which they are applied varies greatly for the different types, and also for different areas of analytical chemistry. The possibilities for their use are so diverse that few generalizations are possible. In some instances, such as differential adsorption and liquid-liquid extraction, the methods are much more widely used in biochemical, agricultural, pharmaceutical, and other areas of organic chemical work than in such general inorganic analysis as the analysis of metallurgical products.

In general, then, partition separations seem to be quite satisfactory for, and in many cases indispensable to, a variety of work. They are particularly useful for organic systems. Use of partition processes is steadily increasing, especially for the isolation of constituents from very complex mixtures. Interest in the development and application of such methods has been stimulated by the success achieved in accomplishing most difficult separations in biochemistry, petroleum research and manufacture, and atomic energy research and production. Investigation of different kinds of partition separation processes and their application is today one of the active areas of research in analytical chemistry.

CHAPTER 11

THE GENERAL PROBLEM OF MEASUREMENT

At this point the final operation of every quantitative chemical analysis, namely, *measurement of the desired constituent(s)*, must be considered. The general objective of this chapter is to consider briefly the principles of measurements, to outline the available methods of measurement, and to consider the problem of naming analytical methods to indicate the kind of measurement used. Before taking up these topics, however, it may be helpful to recapitulate what has been covered in the preceding nine chapters, two of which deal with measurement.

Every analysis starts with the obtaining of a sample. In order for the procedure to be quantitative, the test sample to be analyzed must be measured, usually by mass or volume. Sometimes, of course, this measurement is not apparent, as with measurement of a radiator antifreeze solution, but in such cases measurement of the sample may be considered as having been accomplished in the prior calibration of the reading scale, table, or curve (see the discussion of densimetry in Chapter 19).

In many kinds of materials the desired constituent, or something chemically equivalent to it, can be measured immediately after the sample has been measured, that is, no preliminiary treatment of the test sample or separation of interfering constituents is necessary in order for the subsequent measurement to be accomplished.

Much more frequently, however, such preparative and/or separative treatment is necessary as a preliminary to measurement of desired constituents. Common preparative operations are fusion, dissolution, and control of factors important for the given situation, e.g., *p*H and state of oxidation. Then with complex materials such as granite rocks, which contain some 20 components, the material must nearly always be taken apart sufficiently to render the individual components measurable. For this purpose the analyst applies the methods of separation discussed in Chapters 7 to 10. The most common kinds of separation are volatilization, precipitation, electrodeposition, and partition.

In these premeasurement stages of an analysis, nearly all of the chemistry that may be involved in the overall procedure occurs. It is found in the transformations and/or separations required to remove interfering constituents and to convert the desired constituent, or something chemically equivalent to it, into measurable form. If an analysis is long, tedious, and demanding of skill in the art, almost always these preparatory stages are involved.

PRINCIPLES OF MEASUREMENT

In general, *measurement* is the determination of the number of times a standard goes into the unknown to be measured.[1] Thus, to measure the distance between the end markers of a football field, one might lay the standard yardstick end-to-end from one end boundary to the other. Similarly, the mass of a sack of ore might be reported in terms of the number of kilograms necessary to balance the material on a weighing instrument.

Measurement thus involves determination of the magnitude of some physical property of the system concerned. As illustrations, length and mass have just been mentioned. Other well-known physical properties used in measurement are volume, area, pressure (of gases), and density. To these may be added a variety of optical, electrical, thermal, and other properties.

Since measurement as such involves no process of chemical transformation of matter, the operation is not chemical in a strict sense. It may be considered, rather, as the application of principles of physics and its subdivisions, e.g., mechanics, heat, optics, electricity, and sound.

KINDS AND CLASSIFICATION OF MEASUREMENT

A considerable number of different methods of measurement is now available to analysts, and the number of instruments available for performing the operations is much greater. Since no such comprehensive field can be covered in an elementary book, selections must be made by the author. In analytical terms, this means that the whole area must be sampled. The methods of measurement chosen for consideration in this book are titrimetry, gravimetry, colorimetry, and electrometry. The basis for the nomenclature used is discussed later in this chapter.

As justification for the selections made, the following facts seem relevant: (1) the fundamental importance of gravimetry; (2) the early and continued extensive use of titrimetry and gravimetry; (3) the widespread

[1] Webster's dictionary definition of *measure* is "To compute or ascertain the extent, degree, quantity, dimensions, or capacity of, by a rule or standard."

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prior to measurement, the method is physico-chemical. Thus, determination of the density of a radiator antifreeze solution is physical; but the spectrophotometric determination of manganese in steel, following dissolution, complexation of the iron, and oxidation of the manganese to permanganate, is physico-chemical.

Just as all methods of measurement are physical, they are likewise instrumental. Some kind of instrument or measuring device is necessary in order for a measurement to be made. Listing gravimetric methods as noninstrumental thereby excludes the analytical balance as an instrument, yet in terms of its measuring capabilities, it is one of our finest analytical instruments.

The student may well ask, "What basis of classification, then, is acceptable?" One must answer that none has gained acceptance, even though a rapidly expanding literature makes the need ever more urgent. For those who may be interested in thinking about the problem, several bases for classification are mentioned here, together with references to details.

1. One classification[2] is based upon the distinction between specific and systemic properties of the entity measured. In specific-property methods, one measures a specific property, such as mass or volume, *of* the desired constituent, or of something bearing a known relationship to this constituent. Thus, selenium is precipitated and weighed as such, but silver is precipitated as silver chloride and weighed in this form. In systemic-property methods, one measures a property of a system *containing* the desired constituent. A common example is the determination of specific gravity of a radiator solution consisting of water and ethanol, the alcohol being the desired constituent. Other examples are the determination of the electrical conductivity of a binary alloy, the thermal conductivity of stack gas from a power plant, the refractive index of an aqueous solution of ethanol, and the light-absorptive power of an aqueous solution of permanganate.

2. A second proposed classification[3] is based on the distinction between nondiscriminatory, semidiscriminatory, and discriminatory methods. These types are based upon the possibilities that the measurement may be (a) independent or dependent on the amount of the material present, and (b) independent, or a function of the nature of the substance being measured. Accordingly, one may have methods which are dependent only on the amount or only on the nature of the material being measured, or which depend both upon the amount and upon the nature of the material being present. This basis of classification is outlined and exemplified in Table 11.1.

[2] Mellon and Mellon, *J. Chem. Educ.* **14**, 365 (1937).
[3] Elving, *Anal. Chem.* **22**, 962 (1950).

TABLE 11.1

METHODS OF MEASUREMENTS

Method Is Function of—			
Amount of Material	*Type of Material*	*Type of Method*	*Example*
x		Nondiscriminatory	Balance
	x	Semidiscriminatory	Densimeter
x	x	Discriminatory	Polarograph

The original paper should be consulted for details on the merits, limitations, and applications of each of these types of methods.

3. A third basis[4] rests upon the distinction between static and dynamic property methods. Static properties of any system are those that are characteristic of the system as such, and that do not fundamentally involve external measurement of energy (or particles) passing from or through the system. Such physical properties as mass, volume, density, pressure, viscosity, temperature, as well as magnetic and chemical-reactive properties may be considered to be inherent or "contained" in the system. They do not, fundamentally, require the application or emission of external energy waves or particle waves for their measurement.

Dynamic properties, in contrast, are those for which measurement depends on the motion of energy waves or particles passing through, or originating in, the system. Such phenomena exhibit many characteristic behaviors, and numerous technics have been devised for dealing with them. All optical properties are dynamic, as are those for the entire electromagnetic spectrum. Here, also, may be included measurements of heat conduction, electrical phenomena, sound, and radioactivity. Fundamentally, then, dynamic properties are those that control the transport of waves, whether their nature be electromagnetic, electric, sonic, thermal, subatomic, atomic, or molecular.

The following outline, based upon this last viewpoint, is intended to give an idea of the variety and the number of methods of measurement now available. For each property listed, an appropriate name for the kind of method has been included. Some spellings of these names remain uncertain, e.g., spectrometry or spectrimetry; for consistency, however, all endings are -imetry.

OUTLINE

I. Static Properties
   A. Mass—gravimetry

[4] Patterson and Mellon, *J. Chem. Educ.* **26**, 468 (1949).

- B. Volume—volumimetry
- C. Density—densimetry
- D. Pressure—manimetry
- E. Viscosity—viscosimetry
- F. Temperature—thermimetry
- G. Magnetic properties—magnetimetry
- H. Chemical reactivity
  1. Combining power—titrimetry
  2. Heat of reaction—calorimetry
  3. Speed of reaction—chronimetry

II. Dynamic Properties

- A. Wave motion
  1. Sound—sonimetry
  2. Radio (microwaves)—radiimetry
  3. Radiant energy (infrared, visible, ultraviolet, X-ray)
     - a. Emission—emissimetry
       (1) Flame photimetry
       (2) Emission spectrimetry
       (3) Raman effect—ramanimetry
       (4) Fluorescence—fluorescimetry
       (5) Phosphorescence—phosphorescimetry
     - b. Transmission—transmissimetry
       (1) Absorption—absorptimetry
       (2) Thermal conduction—thermoconductimetry
       (3) Turbidity—turbidimetry
       (4) Optical rotation—optirotimetry
       (5) Refraction—refractimetry
       (6) Diffraction—diffractimetry
     - c. Reflection
       (1) Reflectimetry
       (2) Tyndall effect—nephelimetry
  4. Gamma rays—gammimetry
  5. Cosmic rays—cosmimetry
- B. Particle motion
  1. Atoms and atom groups
     - a. Mass spectra—masspectrimetry
  2. Subatomic particles
     - a. Transmission of electrons—electrimetry
       (1) Conductivity—conductimetry
       (2) Potential—potentiimetry
       (3) Current—currentimetry
       (4) Capacity—dielectrimetry
       (5) Diffraction—electron diffractimetry

b. Nuclear particles—radioactimetry
   (1) Beta particles
   (2) Alpha particles
   (3) Neutrons

4. Other possibilities of classification have been suggested. Perhaps the most comprehensive is that of Serfass *et al.*,[5] which takes into account such items as the mechanical handling of the sample, biological testing of activity, and purely mechanical tests.

NOMENCLATURE

Current nomenclature of analytical methods as a whole is generally chaotic. To substantiate this statement, the author has arranged the following outline[6] from examples taken from well-known publications:

PROCEDURE DESIGNATED IN TERMS OF—

1. The originators(s) of the method.
   a. The individual(s); e.g., Kjeldahl method.
   b. The institution or laboratory, e.g., Harvard, or Bureau of Mines method.
2. The organization approving the method.
   a. Name only, e.g., U.S.P. (U.S. Pharmacopoeia) method.
   b. Name and status of adoption, e.g., ASTM (American Society for Testing Materials) official or tentative method.
   c. Name and applicability, e.g., AOAC (Association of Official Agricultural Chemists) general or special method.
   d. Name and number, e.g., APHA (American Public Health Association) method I.
3. The kind of material analyzed, e.g., steel-analysis method.
4. The physical state of the samples, e.g., gas-analysis method.
5. The general conditions maintained, e.g., wet or dry method.
6. The magnitude or scale of operations used, e.g., micro or macro method.
7. The kind of general physical method used, e.g., mechanical, electrical, or ultrasonic method.
8. The effect or action of the desired constituent, e.g., polarization or emanation method.
9. The instrument used.
   a. In preliminary treatment of sample, e.g., Parr bomb method.
   b. In separation of the desired constituent, e.g., vacuum-oven method.
   c. In measurement of the desired constituent, e.g., refractometer method.

[5] Serfass, et al., *Anal. Chem.* **22**, 966 (1950).
[6] Mellon *et al.*, *Anal. Chem.* **19**, 931 (1947).

10. The principal reagent used.
    a. In preliminary treatment of the sample, e.g., peroxide-fusion method.
    b. In separation of the desired constituent, e.g., nitron method.
    c. In measurement of the desired constituent
        (1) Class of reagents, e.g., acidimetric method.
        (2) Specific reagent, e.g., iodimetric method.
11. The property measured in determining the desired constituent.
    a. A specific property, e.g., gravimetric method.
    b. A systemic property, e.g., densimetric method.
12. The principal single operation or process used.
    a. In preliminary treatment of the sample, e.g., fusion method.
    b. In separation of the desired constituent, e.g., electrolytic method.
    c. In measurement of the desired constituent, e.g., titration method.

Since there is as yet no generally accepted or official usage, the author has used in this book a nomenclature designed to indicate both the nature of the operation of separation (if one is necessary) and the kind of measurement. This usage is functional in the sense of naming the two principal kinds of things done in the method. One familiar with the art and science of analysis is then in a position to understand at least something of what is done. In many cases, too, he may evaluate results to the extent that he knows the peculiarities of particular kinds of procedures.

To indicate the kind of separation, the terms used in Chapters 7 to 10 are appropriate. These include volatilization, condensation, precipitation, dissolution, electrodeposition, extraction, absorption, adsorption, and others.

To indicate the kind of measurement a word or prefix for the property measured may be combined with the ending -metric. The related endings -metry and -meter apply, respectively, to the area or operation concerned and to the instrument used.

As examples of names for combinations of methods of separation and measurement the following are typical: volatilization-volumetric; precipitation-gravimetric; electrodeposition-titrimetric; and extraction-absorptimetric. The application and significance of such names will be evident in succeeding chapters.

It may be mentioned that such a functional nomenclature is roughly analogous to that used by the International Union of Pure and Applied Chemistry for naming organic compounds.

CHAPTER 12

TITRIMETRY: GENERAL PRINCIPLES

One of the most widely used methods of analytical measurement is based upon accomplishing a reaction between (1) a solution of known chemical reactivity or value and (2) a solution of the desired constituent, or something chemically equivalent to it. In practice, the operation involves determination of the amount of a solution necessary to complete the reaction. The process is known as *titration*. Titrimetry is the subdivision of quantitative analysis which includes all such methods.

The term "titrimetric," rather than the older term "volumetric," has been adopted here for two reasons: (1) it indicates definitely the kind of measurement to which reference is made, and prevents confusion with certain other methods (see Chapter 19 for volumetric measurements); (2) it provides for methods employing titrations made either by volume or by weight.

Titrimetric measurement is dependent upon at least three items: (1) an arrangement, usually a measuring vessel, by means of which the amount of titrant, and therefore the process of titration, is controlled; (2) a titrating or standard solution, with which to accomplish the titration; and (3) a chemical reaction of such a nature that the reactivity of the standard solution toward the desired constituent can be measured. The specific requirements of such reactions are considered in a later section.

Several distinct kinds of reactions are employed in titrimetry; the most common are neutralization, oxidation-reduction, precipitation, and complexation. Occasionally, the processes are classified as ion-combination and electron-transfer reactions. The former usually include neutralization, precipitation, and complexation reactions, and the latter involve oxidation-reduction processes. The theory of the various types of reac-

tions, as well as the procedures involved in their use, are discussed in subsequent chapters.

Comprehensive monographs on titrimetric methods describe other, more specialized types of reactions.[1]

We may now consider some important items connected with the process of titration. Three of these, as indicated, are of special significance from the standpoint of the general treatment given in this chapter: (1) measurement of the standard solution, or titrant; (2) preparation and standardization of the standard solution; and (3) conditions necessary for using a reaction as the basis for titrimetric measurement.

The usual process of titration involves addition of a solution of known reacting value, the titrant, to the sample solution. In subsequent discussion the term "titrant" refers to the standard solution. Occasionally the sample solution is used to titrate a known amount of the standard solution.

MEASUREMENT OF THE TITRANT

By Mass

The most precise titrimetric measurements are made by weighing the amount of titrating solution used. For this purpose several forms of vessels, known as *weight burets,* have been devised. One of them is illustrated in Figure 4.3,[2] page 47.

This procedure requires that the solution be prepared on a weight basis (discussed later), and the process of titration therefore becomes relatively slow. However, precise work necessitates this type of preparation, unless one has equipment and facilities for careful control of temperature, and highly precise and accurately read volumetric apparatus. As advantages for the use of weight burets, the following points may be mentioned: (1) calibration is unnecessary, since graduated vessels are not needed; (2) cleaning need be less careful, as drops clinging to the inside surface of the vessel do not affect the results; (3) ordinary changes of temperature do not affect the results; (4) there are no drainage errors; and (5) when the stopper is closed evaporation of the solvent is impossible.

By Volume

The much more common practice of titrimetric measurement is to use the volume-measuring vessels illustrated in Chapter 4. The general purpose and manner of handling of such equipment have already been discussed.

[1] See Kolthoff and Stenger, *Volumetric Analysis,* Interscience, 1942.
[2] Friedman and La Mer, *Ind. Eng. Chem., Anal. Ed.* **2**, 54 (1930).

It may be well to emphasize that precise work with such ware requires careful attention to various details. Assuming that the calibration has been properly done, the student should not forget the following considerations: (1) the calibration corrections should be applied unless they are within the tolerances of the National Bureau of Standards, or unless the accuracy of the work in hand does not require their application; (2) all ware should be clean, i.e., the solution should drain uniformly from the glass walls without leaving discrete drops behind; (3) vessels should be either dry (and clean) at the start of analysis, or be rinsed out with the solution to be measured in order to prevent dilution; and (4) excessive changes in temperature should be avoided, unless they are allowed for in the manner suggested in the next section.

Temperature effects. Vessels for titrimetric work by volume are correct only at the temperature for which they are calibrated. The National Bureau of Standards specifies that this temperature be 20°. Changes of temperature in the laboratory produce two effects: (1) ordinary volumetric ware, made of glass, expands with rise of temperature; and (2) the solutions measured in this ware are subject to a similar change through the working range of temperatures. Unfortunately, the two changes do not compensate for each other. The coefficient of cubical expansion for glass differs from those for aqueous solutions in that it is much smaller and is linear for the range of temperatures concerned.

Analysts have determined experimentally that the magnitude of the change in volume for many dilute aqueous solutions having a concentration in the neighborhood of 0.1 N or less is approximately 0.02 per cent per degree C. A change of 15° would then amount to about 0.3 per cent, an error easily possible if the solution is prepared in winter in a cool laboratory and used later on a hot summer day. If one aims at a summation of errors of 0.1 per cent, this factor is of considerable importance.

In another place the author directed attention to some of the possibilities that have been proposed[3] for eliminating or reducing the errors from this source. Except for the time required, use of weight burets is the best suggestion. The solutions are then made on a weight basis, and a titer may be determined per gram (or per milligram) of titrant rather than per milliliter.

Another suggestion is to use flasks and pipets having a series of graduation marks instead of the single mark now found. Knowing the temperature of the liquid to be measured, one could select the corresponding mark. Such ware is not commercially available insofar as the author knows. For the buret, use of a chart showing the combination of tem-

[3] See Mellon, *Ind. Eng. Chem., Anal. Ed.* **2**, 260 (1930).

perature and graduation errors would be necessary. This plan assumes the use of an "average" solution.

A practice which largely reduces error as a result of temperature effects is to use a series of correction factors based upon the resultant of the changes in the container and the "average" solution. Then if the temperature of the solution is known at the time of measurement, its volume (corrected to 20°) is obtained by multiplying the volume read by the appropriate factor. Table 12.1 gives a series of factors calculated for this purpose.

TABLE 12.1

FACTORS FOR TEMPERATURE CORRECTIONS

Temp.	*Factor*	*Temp*	*Factor*	*Temp.*	*Factor*
15	1.00077	22	0.99961	29	0.99793
16	1.00063	23	0.99940	30	0.99765
17	1.00049	24	0.99918	31	0.99736
18	1.00034	25	0.99895	32	0.99706
19	1.00018	26	0.99871	33	0.99675
20	1.00000	27	0.99846	34	0.99643
21	0.99981	28	0.99820	35	0.99610

A variation from 20° will cause no error in calculation, of course, if the standard solution is made and used at the same temperature.

PREPARATION OF THE STANDARD SOLUTION

Reference has already been made to the standard solution. If calculations are to be made on the basis of the amount used in a given titration, one must know its concentration or chemical reactivity accurately. The requisite knowledge is (1) the amount of solute contained in unit amount of the solution, or (2) the amount of unknown with which this unit amount of solute will react, or to which it is chemically equivalent.

Definitions

As these reaction values may be specified in several ways, understanding of the definitions concerned is necessary.

A *standard solution* is one of known reacting value. In analytical chemistry this known value is usually specified in one of the following terms: concentration per unit volume or mass, molarity, formality, normality, or titer. Percentage composition is used rarely for quantitative specification. These terms are briefly defined here and are discussed later.

Concentration per unit volume is conventionally expressed in grams of solute per liter or milliliter of solution (many teachers prefer milligrams per milliliter of solution). If the titrant is weighed, the designation is likely to be grams of solute per gram of solution.

A *molar solution* is one containing 1 gram-molecular weight (1 mole) of the reactant per liter of solution. This designation should not be confused with *molal,* a term used in physical chemistry to specify a solution containing 1 gram-mole of solute per 1000 g of solvent. A millimole is one thousandth (0.001) of a mole.

A *formal solution* is one containing 1 gram-formula weight of the reactant per liter of solution. It is usually identical in concentration with a molar solution, but there is no specification of the molecular or ionic species existing in solution.

An *equivalent weight* of a reactant is the mass chemically equivalent to 1.0080 g of hydrogen. This value for hydrogen refers to the naturally occurring isotopic mixture of the element and not to any one of the several isotopic species. A milliequivalent weight is one thousandth (0.001) of the equivalent weight.

Using the value 1.0080 g for hydrogen, along with its reactive values expressed in the equations

$$\begin{array}{rcl} H^+ + OH^- & \rightarrow & H_2O \\ 1.0080 \quad \approx & & 17.0080 \end{array}$$

$$\begin{array}{rcl} HCl + NaOH & \rightarrow & NaCl + H_2O \\ 36.465 \quad \approx & & 40.008 \end{array}$$

$$2\ HCl + Na_2CO_3 \rightarrow 2\ NaCl + H_2O + CO_2\uparrow$$

$$\frac{2(36.465)}{2} \approx \frac{106.00}{2}$$

$$H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$$

$$\frac{98.022}{2} \approx \frac{106.00}{2}$$

one may calculate that the various reactants have the following equivalent weights, in grams: $H^+ = 1.0080$; $OH^- = 17.0080$; $HCl = 36.465$; $NaOH = 40.008$; $Na_2CO_3 = 53.00$; $H_2SO_4 = 49.01$.

A *normal solution* is one containing 1 gram-equivalent weight of solute per liter of solution, or 1 milliequivalent per milliliter.[4]

The *titer*[5] of a standard solution is the amount in grams of any substance with which a unit amount of solution (usually 1 ml, but occa-

[4] In gas analysis a normal ("gas-normal") solution is one in which 1 ml is equivalent to 1 ml of the gas measured dry under normal temperature and pressure.

[5] One author uses the term "titer" to refer to grams of solute per milliliter of titrant.

sionally 1 g) will react, or to which it is chemically equivalent. Thus, according to the following equations, 1 ml of normal (1.0000 N) hydrochloric acid is equivalent to 0.04001 g of sodium hydroxide or to 0.05300 g of sodium carbonate, assuming complete neutralization of the carbonate

$$\begin{aligned} HCl\ (36.465) + NaOH(40.008) &\rightarrow NaCl + H_2O \\ 2\ HCl\ (36.465) + Na_2CO_3(106.00) &\rightarrow 2\ NaCl + H_2O + CO_2\uparrow \end{aligned}$$

whence

$$HCl \eqsim NaOH \eqsim Na_2CO_3/2$$

$$\frac{36.47}{1000} \eqsim \frac{40.01}{1000} \eqsim \frac{106.00}{2 \times 1000}$$

$$0.03647 \eqsim 0.04001 \eqsim 0.05300$$

A *percentage solution,* if made on a weight basis, is specified in terms of grams of solute per hundred grams of solution.[6] Common laboratory reagents are often prepared on the percentage basis.

Calculative Merits of the Systems Used for Expressing Concentration or Reactivity

The system used for expressing the chemical value of a standard solution determines the calculations involved in the use of the solution. The following sections bear upon some of the more important points concerned in the calculations.

Concentration per unit volume. In the case of concentration per unit volume, the concentration is usually given in grams of solute per milliliter of solution. Thus, a solution of hydrochloric acid might contain 0.003720 g of hydrogen chloride per milliliter (g/ml). If this solution is used to titrate a solution of sodium hydroxide, the equation for the reaction is

$$HCl\ (36.47) + NaOH\ (40.01) \rightarrow NaCl + H_2O$$

This equation shows that 1 gram-mole of hydrogen chloride (36.47 g) reacts with 1 gram-mole of sodium hydroxide (40.01 g). Then 1 ml of the solution, containing 0.003720 g of hydrogen chloride, would react with

$$0.003720\ g \times \frac{40.01}{36.47} = 0.004081\ g$$

of sodium hydroxide.

This solution of acid may be used to titrate the sodium hydroxide in a sample. If the results are to be expressed in terms of percentage of sodium hydroxide, one uses the relationship

[6] Some authors use the expression (incorrectly) in other ways, as, for example, grams of solute per 100 ml of solvent.

$$\frac{\text{ml of HCl} \times 0.003720 \times \dfrac{\text{NaOH (40.01)}}{\text{HCl (36.47)}}}{\text{weight of sample}} \times 100 = \text{per cent NaOH}$$

Use of a titrant value expressed in this way is generally recommended when (1) a solution is not stable, (2) it cannot be made by direct weighing of the solute, and (3) it is to be used for only a few measurements. In any of these cases one is unable, or does not find worth while, making a titrant with a predetermined value, such as those discussed later.

Molar and formal systems. In quantitative analysis the molar system has been relatively little used, although it has distinct merit.[7] Most important is the fact that little uncertainty can arise over what is meant by a solution containing 1 gram-molecular weight per liter. Any desired titer for such a solution, in terms of a given substance, is easily calculated from the equation showing the chemical reaction involved.

The formal system, which is similar in general practice to the molar system, is considered by some to have certain advantages, the main one being that there is no uncertainty as to formula weight in a given case.

Normal system. During the development of titrimetric methods through more than a century, thinking in terms of the normal system has become almost instinctive with chemistry teachers and many industrial analysts. This situation is probably attributable to the belief that a solution containing 1 equivalent of reactant per liter of solution has the following merits: (1) 1 ml is chemically equivalent to 1 ml of any other normal solution; (2) 1 ml is equivalent to 1 milliequivalent of any substance; and (3) the normalities of solutions equivalent to each other are inversely proportional to their respective volumes. Although these relationships are often true, they are not necessarily so. In view of what is stated later concerning the variability of certain equivalent weights, these generalizations should be used only after their applicability in a specific case has been ascertained.

As with solutions expressed on the molar basis, two methods are used to designate concentration. If the solution contains a simple fraction of an equivalent weight per liter symbols such as $N/10$ are common. Such a symbol may or may not indicate that the concentration is reliable to four significant figures. If it does, 1 ml of $N/10$ hydrochloric acid, for instance, would contain 0.003647 g of hydrogen chloride. When the concentration is not a simple fraction of the equivalent weight per liter, the normality is expressed best in a decimal form, as 0.1058 N.

The assumed advantages of the normal system have been stated. Be-

[7] Fales, *Inorganic Quantitative Analysis*, Century, 1925, is one of the few texts recommending the molar system.

cause of these, analysts have generally considered that solutions expressed on the normal basis are most convenient when a number of different kinds of constituents are to be determined with the same titrant. Thus, sodium hydroxide may be used to titrate a large number of acids.

The distinct disadvantage in this system lies in the possible uncertainty as to what is meant if certain solutions are said to be normal. The difficulty centers in the fact that the equivalent weight of various reactants differs in different reactions. To indicate something of this uncertainty, examples are cited in each of the following three chapters.

The author cannot too strongly stress, of course, that calculations in any practical case are predicated upon the use in the titration of particular reactions. The equivalent weight of sodium hydroxide is invariant in neutralization reactions. In contrast, that of sodium carbonate may be either the same as, or one half of, the molecular weight, depending upon the reaction used (see page 197).

Titer system. If the value of a titrant is specified in terms of something with which the solution reacts, or to which it is chemically equivalent, two simple bases are available: (1) the titer system; and (2) the "factor" system.

The titer (or equivalency) of a titrant may be defined as the amount of substance (usually expressed in grams) with which a unit amount of the titrant will react, or to which it is chemically equivalent. This unit amount is usually 1 ml, but it may be on a mass basis, such as 1 g. As an example, we may consider a standard solution of hydrochloric acid containing 0.007293 g/ml (7.293 g/liter). Then its sodium hydroxide and nitrogen titers are, respectively, 0.008001 g and 0.002802 g.

$$\text{Titer for NaOH} = \text{g HCl/ml} \times \frac{\text{eq. wt. NaOH}}{\text{eq. wt. HCl}}$$

$$= 0.007293 \text{ g} \times \frac{40.01}{36.47}$$

$$= 0.008001 \text{ g}$$

or

$$= N_{(\text{HCl})} \times \text{meq.wt.}_{(\text{NaOH})}$$

$$= \frac{7.293}{36.47} \times 0.04001 \text{ g}$$

$$= 0.008001 \text{ g}$$

$$\text{Titer for N} = 0.2000 \times 0.01401 \text{ g}$$

$$= 0.002802 \text{ g}$$

These values may be spoken of as the titers of the acid in terms of sodium hydroxide and of nitrogen. The acid will *react with* the hydrox-

ide, but not with the nitrogen. However, from our knowledge of ammonium hydroxide, we know that one nitrogen is therein equivalent to 1 mole of hydrochloric acid. Consequently, we can calculate the amount of nitrogen to which 1 ml of the acid is equivalent.

The use of titer values is one of the simplest procedures to follow in calculating percentages. For example, the $T_{(NaOH)}$ calculated for the solution of hydrochloric acid containing 0.007293 g/ml was 0.008001 g. Then the expression for calculation of results in the use of this acid for titrating sodium hydroxide is

$$\frac{\text{Volume of HCl} \times 0.008001}{\text{Weight of sample}} \times 100 = \text{per cent of NaOH}$$

If the sample is made numerically equal to 100 times the titer, or 0.8001 g, the volume of titrant equals the percentage directly.

"Factor" system. A method related to the titer system employs a factor. Its use involves weighing out equal amounts of the unknown sample and of the standard used to check the titrant. The percentage of the constituent contained in the standard sample is divided by the volume of the titrant used in order to obtain the "factor." Then, in titrating unknown samples of the *same* weight, the analyst multiples the volume of titrant used by this factor to obtain the desired percentage of constituent.

Such a procedure has its chief use in industrial laboratories where conditions are such that many routine analyses are performed by technicians or "determinators."

Methods of Preparation

Although not the most economical, the simplest method of procuring standard solutions is to purchase them already prepared from chemical supply houses. For many years commercial firms have sold prepared, dilute standard solutions. Also for a number of commonly used titrants, one may obtain definite amounts of the solute weighed out in sealed glass vials.[8] The only procedure left for the analyst is to wash the material into a flask, and dilute it to the mark. A word of caution should be given those who might be inclined to place unquestioned reliance upon all such materials. It is wise to be skeptical of the value given wherever there is likely to be instability of the system because of action of any of the factors to be mentioned later in the discussion of the preservation of solutions.

[8] Examples of such materials are sold under the trade names "Acculute" (United States), "Fixanal" (Germany), and "Analar" (England).

Whenever the analyst prepares his standard solution, as he will in most cases, one of two general methods is used. If the solute is of definite and known composition, if it can be handled quantitatively, and if it is satisfactory otherwise, the simplest procedure is to measure out directly, usually by weight, the calculated amount and dilute it to the desired volume. Sodium carbonate, sodium oxalate, sodium chloride, potassium dichromate, and a number of other substances can be handled in this way. In general, they meet, or approach the requirements of primary standards discussed on page 84. Solutions prepared from such materials are made to have some particular value or concentration. It is equally easy, for example, to make a solution of potassium dichromate with a normality of 0.1000 or a titer of 0.005000 g in terms of iron.

The second method is used for materials not having the characteristics just mentioned, since such substances cannot be measured accurately. In this method, the analyst prepares a solution with approximately the desired concentration and then carefully determines its value by a reliable method, such as one of those discussed subsequently. If a specific concentration is desired, the solution is made a little too concentrated, the concentration determined, and then enough solvent added to effect the necessary dilution. Experimental application of these different procedures will be found in succeeding chapters.

If the concentration is expressed in terms of the solution itself, the same systems are used as in the comparable situation for solutions not made to an exact concentration, that is, in terms of grams per milliliter, molarity, or normality. If the concentration is to be in terms of something with which the solution will react, or to which it is chemically equivalent, the concentration is usually made so that 1 ml is equivalent to a simple fraction of a gram of the desired constituent, such as 0.005000 g. This means that the standard solution is made to have a specific titer.

As stated previously, such simple titers are usually recommended when a given titrant is to be used for a single constituent in many samples. Thus, if an acid has a sodium carbonate titer of 0.005000 g, the use of 0.5000-g samples eliminates further calculations, since each milliliter of acid used equals 1 per cent of sodium carbonate. Of course a solution having a simple titer for one substance will not have the same value for any other substance unless their equivalent weights should happen to be the same. However, the titers of a given solution for two different substances have the same ratio as the equivalent weights of the substances. Accordingly, if the titer T for one substance x is known, the titer for another substance y can be readily calculated

$$T_y = T_x \times \frac{\text{eq. wt. of } y}{\text{eq. wt. of } x}$$

Unjustified Specific Titers

Consideration of the practical problems involved shows that preparation of solutions with specific values is often a waste of time unless the solute can be weighed directly. This is true for situations such as the following:

1. The solution is to be used only a few times. In the titration of two samples of soda ash, for example, the use of whatever titer the acid happens to have for sodium carbonate takes less time than to bring the concentration of titrant to a specific value. Each milliliter of solution can be made to read 1 per cent of sodium carbonate by taking a sample weight equal to 100 times the titer in terms of sodium carbonate.

2. The solution is one in which it is difficult to make dilutions without introducing some undesirable constituent into the system. Thus, definite volumes of $N/20$ sodium hydroxide solution free of carbonate may be specified for making buffer solutions. It is most convenient to make the solution approximately $N/20$, determine the normality, and then use a conversion factor to calculate the volume of solution equivalent to some required volume of $N/20$ solution (see problems, page 633).

3. The solution is not stable. Solutions such as ferrous sulfate, the values of which change more or less rapidly, cannot be relied upon to have a specific titer for more than a few days.

4. The solution is to be used with different indicators giving different end points. On titrating sodium hydroxide solution with an acid, for instance, one obtains a different value for each indicator having a different *p*H range. Therefore, a solution made exactly 0.1000 N for methyl orange does not have this value for phenophthalein (see Exercise, 25.6, page 411).

Selection of Concentration

We now come to another aspect of the problem of concentration of titrants. Whenever a standard solution is to be prepared, the analyst must decide on the range of concentration within which measurement is desirable. For example, the question might be whether the solution should be 1.0000 N, 0.001000 N, or some intermediate value. Actually, the two extremes given are almost the outside limits employed, even in special cases. Generally the concentration lies in the range 0.05 to 0.2 N, with approximately 0.1 N being the most widely used.

Brief consideration may be given to some of the factors governing the selection of some workable concentration. The first factor to be considered is the sharpness of end point desired, when a color indicator is used. Near the end of the titration a series of stepwise color changes

occurs, the magnitude of each change being proportional to the amount of reactant in each drop of solution added. Obviously, the more concentrated solutions should be used to produce more marked changes of color per drop of titrant.

A second factor is the relation of the concentration of the solution to the limitations of measuring apparatus. The more dilute the solution, the smaller will be the reading errors on a percentage basis, since a larger volume of dilute solution will be required and the absolute reading error (position of meniscus) is approximately constant for a given buret. Requirement of high precision would point to the use of dilute solutions, although excessive dilution may introduce a significant error in locating the end of the titration.

In a technic that is used occasionally for precise work, most of the titrant required is added from a weight buret. Then the last portions of titrant are added from a micro buret of 3- or 5-ml capacity, which can be read with much better accuracy than the usual 50-ml buret.

In general, for a given precision in measuring the amount of titrant consumed, the product of the concentration of standard solution and the the accuracy of reading the buret should be about a constant value.

A third factor is the adaptation of the solution to specific analytical ends. Several examples illustrate such adaptation. If the sample is quite dilute with respect to the constituent to be titrated, a dilute standard solution should be used in order that a reasonable volume reading on the buret may be obtained. Thus, $N/50$ acid is generally specified for determining the alkalinity of water. For some reactions it may be desirable, from mass-law considerations, to use more concentrated titrants. To determine the alkalinity of limestone, acids at least $N/5$ are recommended. The time of dissolution is too long with less concentrated acids.

With direct reading solutions, where the number of milliliters of titrant used equals the percentage of desired constituent, the concentration of the standard solution should be such that 1 ml has a titer, in terms of the desired constituent, of 0.01 of the weight of sample used, as shown by the expression

$$\frac{\text{Volume of titrant} \times \text{titer}}{\text{Weight of sample}} \times 100 = \text{per cent}$$

the titer and weight of sample being expressed in grams and the volume in milliliters. Most conveniently, a single weight piece, such as 0.5000 g may be used in measuring the sample. The standard solution is then made so that 1 ml is equal to 0.005000 g of desired constituent.

It is evident from the above discussion that many cases will require

the selection of a concentration of titrant that is a compromise with respect to several important factors.

Preservation of Solutions

Although solutions may be made for use and then discarded within a short time, they are usually kept until they are consumed. A number of them retain their original concentration more or less indefinitely (sodium chloride and sulfuric acid, for example). A solution of potassium dichromate has been reported to show no change in 25 years. Many solutions, however, are not stable. In some cases, the analyst may inhibit or greatly retard the reactions that produce changes in concentration. All solutions, of course, are subject to evaporation of solvent unless kept in closed systems. Strongly alkaline solutions act on glass containers to become more alkaline, and they absorb carbon dioxide from the air to reduce their normality when phenolphthalein is used as the indicator. Paraffining the inside of the bottle sometimes prevents the former action; entrance of carbon dioxide may be prevented by a guard tube containing soda lime (see Figure 25.1) on the container and on the buret.

Photochemically sensitive solutions, such as silver nitrate, must be kept away from light, or in containers that filter out the active radiant energy. Solutions of sodium thiosulfate are acted on by sulfur-liberating bacteria and by acids. Solutions of iodine in aqueous potassium iodide slowly decrease in concentration, presumably from a reaction between the iodine and the solvent. Potassium permanganate solution is relatively stable only when carefully freed of manganese dioxide and protected from light and organic matter. Ferrous sulfate solution oxidizes quite rapidly in contact with air, but the speed of oxidation is much reduced in the presence of sulfuric acid or of metallic aluminum. Chromous and titanous solutions are even more easily oxidized.

STANDARDIZATION OF SOLUTIONS

Standardization of solutions usually involves determining their concentration in terms of grams per milliliter, molarity, normality, or a titer. Adjustment may be made by dilution with solvent if the solution is too concentrated. Some of the methods of standardization frequently used are presented in the sections following.

Gravimetric Methods

A procedure much used for standardization of solutions is weighing directly the material to be dissolved. If the substance is a primary standard, this is the most desirable method. Weighing errors can be

made negligible. An alternative procedure is to weigh some product obtained from the solution, which bears a definite and known relationship to the solute. The compound so obtained may be the solute itself, as would be the case if one evaporated a measured portion of a solution of sodium chloride. More often some compound having properties requisite for accurate weighing must be formed. A solution of a magnesium salt, such as the chloride, could be so standardized by evaporating a measured portion with an excess of sulfuric acid and weighing the ignited magnesium sulfate. A solution of hydrochloric acid can be standardized very accurately by precipitating silver chloride from a measured portion by means of silver nitrate. Using 25 ml of the acid, the analyst calculates the molarity of the solution according to the expression

$$M = \text{wt. of AgCl} \times \frac{\text{HCl (36.47)}}{\text{AgCl (143.35)}} \times \frac{1}{25} \times \frac{1}{0.03647}$$

Occasionally an analyst prefers such a precipitation-gravimetric process.

Titrimetric Methods

With the exception of direct weighing of the solute, the generally preferred method of standardization is based on titrimetric comparison of the solution with a standard.

Before presenting the titrimetric methods themselves, however, the subject of standards should be considered briefly. Ultimately, such titrimetric methods depend upon reference to some substances of definite and known composition called *primary standards*. To be suitable for this purpose, these materials should have the following characteristics: (1) reasonable ease of preparation and accurate reproducibility; (2) easily determinable purity; (3) stability under ordinary working conditions; (4) usability, without elaborate apparatus or manipulation; and (5) as great precision in standardization of the given solution as that required in the use of the solution. Additional desirable properties for primary standards are that they (1) have a high equivalent weight; (2) be readily soluble in water (or ethanol); (3) be free of interfering products, or have them in the same proportion as the samples to be titrated; and (4) be free of color when dissolved, if an indicator is to be used in titrating them.

The important contribution of the National Bureau of Standards in this direction deserves special comment. The N.B.S. Circular No. 398 and its supplements describe the work of the Bureau, including the general nature of its program and its purpose in preparing and distributing standard analyzed samples. A list of the substances available with their prices

is included. The list of primary standards for general titrimetric work includes benzoic acid, potassium hydrogen phthalate, arsenious oxide, sodium oxalate, and potassium dichromate. Altogether there are some 200 of these substances, including ores, steels, nonferrous alloys, ferroalloys, and others. The method of analysis is given on the certificate accompanying the report[9] for each sample. As a basis of reference these standards have served, and continue to serve, a very important function in analytical work.

Comparison procedures. In one titrimetric method the solution to be standardized is titrated against another solution of known concentration. Preferably the latter is one prepared directly from a primary standard, although often it may have to be one not checked so directly. Each intervening step brings in the possibility of error. In order to check a solution of hydrochloric acid, a common practice is to prepare a solution of sodium carbonate, usually $N/10$ or $N/5$. Portions of 25 or 50 ml are then titrated with the acid. It may be noted that in this case only a single portion of carbonate, that required for preparing the standard solution, need be weighed.

In another method, several separate portions of the standard are weighed, each in sufficient amount to require at least 30 ml of the titrating solution. Usually portions of 0.3 to 0.4 g of sodium carbonate are used with hydrochloric acid. Although a little more time is required for weighing several portions of standard, advantages may be noted. Unless exactly equal amounts are weighed, different volumes of solution will be required to react with them. This eliminates any tendency in reading the buret to see an end point where one wants to see it in order to obtain checking results. For materials that are not stable when dissolved, such as ferrous ammonium sulfate, weighing separate portions into dry flasks is the recommended practice.

Practical points. In the standardization or preparation of titrimetric solutions several points of technic should be kept in mind in order to minimize errors of manipulation. Among these, the following may be mentioned:

1. Make the errors of measurement relatively negligible by using sufficient material, whether measured by weight or volume. Preferably the amounts should exceed 0.2000 g and 20.00 ml. With respective reading uncertainties of ± 0.0002 g and ± 0.02 ml, the amounts to be measured are large enough to make possible achievement of an error within 0.1 per cent of the amount measured.

2. Use measuring instruments that conform to N.B.S. specifications.

[9] See page 366 for an example of a report.

3. Apply the principle of compensating errors if necessary and possible. Two examples will illustrate this practice. If an indicator shows marked differences in colorimetric characteristics under different sources of illumination, keep lighting conditions relatively constant during standardization and use of the solution. The same indicator should be used in standardization and use of a solution. A very important example is the practice of standardizing a solution against a known sample of the substance for which the solution is to be used, and which contains any interfering constituents in amounts approximating those found in the unknown. N.B.S. alloy steels are examples of samples used for such purposes.

Other Methods

Theoretically, at least, one might use a number of the other methods of measurement mentioned in the outline in Chapter 11, insofar as they might be applicable to the system under study. One would not expect, for example, to apply a colorimetric method if no color was to be measured.

As an application of such methods, however, we may consider the determination of the specific gravity or refractive index of a solution of hydrochloric acid. Either of these two measurements can be made, under carefully controlled conditions, with sufficient precision and accuracy that the data may be used for calculating concentration. However, the requirements for reliability, in apparatus and operating technic, are too exacting for ordinary work.

Adjustment of Concentration

As already stated, a solution with a specific normality or molarity, such as 0.1000, usually offers no advantages in the calculation of percentages of desired constituents. Use of the titer value is the simpler process. Also, it has been mentioned that a conversion factor can be applied to calculate volumes of any particular solution equivalent to some given volumes of a solution having a simple, exact normality.

If, for any reason, a titrant must be diluted to have some specific value, the solution must first be made too concentrated, then standardized, and then diluted to the required value. After standardization, the process of dilution may be accomplished by two general methods.

In the first method, the analyst starts with a definite volume of solution, the volume of water to add per liter of solution being calculated according to the expression

$$\left(\frac{\text{Present value}}{\text{Desired value}} \times 1000\right) - 1000 = \frac{\text{ml of } H_2O \text{ to add}}{\text{liter of starting soln.}}$$

Unless the volume of water to add is small, two practical difficulties may be encountered in accomplishing the dilution. Because of forces resulting in contraction or expansion, one may not obtain a total volume equal to the sum of the volumes of solvent and solution being diluted.[10] This difficulty may be avoided by a preliminary approximate dilution, restandardization, and recalculation of the solvent to add. The N.B.S. straight-neck flasks do not provide much space for the addition of solvent. The Giles type of flask (see Figure 4.1B, page 45) provides adequate space for such dilution and, in addition, the auxiliary bulb provides enough solution above the main graduation mark for standardization.

In the second method, the analyst calculates the amount of solution to be diluted to give a definite final volume of the desired concentration, e.g., 1 liter. His calculation is made according to the expression

$$\frac{\text{Desired value}}{\text{Present value}} \times 1000 = \text{volume of starting solution to dilute to 1000 ml}$$

The method avoids contraction or expansion effects, but volumes of solution such as 919.3 ml, may be encountered which may not be conveniently measured.

To make the calculations in either case, the value may be expressed in terms such as grams/milliliter, normality, molarity, equivalent volumes, titer, or other suitable basis.

REACTIONS SUITABLE FOR TITRIMETRIC MEASUREMENT

In view of the general popularity of titrimetric methods in industry, one unfamiliar with the chemistry of the different chemical elements must wonder why lengthy methods of other kinds are ever used. In reply, the author may state that certain precipitation-gravimetric methods are being used out of necessity rather than because of any special attractiveness they have for analysis. Rapid titrimetric methods, if available, would be preferred in place of many lengthy methods now used.

Requirements of Titrimetric Reactions

To be satisfactory for general work, titrimetric methods must be based upon chemical reactions having certain characteristics, the most important of which are summarized here.

[10] To demonstrate such effects, add to a 200-ml volumetric flask (1) 100 ml of water and 100 ml of 95 per cent ethanol, and (2) 100 ml of water and 100 ml of concentrated ammonium hydroxide.

1. The reaction must proceed essentially to completion.[11] Some of the most common types meeting this requirement are characterized by the formation of (a) a slightly dissociated product, (b) a gaseous product which escapes from the system, (c) an insoluble precipitate, and (d) a species of sufficiently different oxidation potential.

2. The reaction must be stoichiometric. This implies that it should proceed according to the equation for the reaction, in only one direction, and without interference from side reactions.

3. The reaction must reach equilibrium with sufficient speed. Much of the value of titrimetric methods depends upon this factor.

4. The reaction must be such that one can detect the completion of the titration.

Back Titrations

In many cases the direct reaction between the titrant and the desired constituent is not suitable because one or more of the above requirements is not met. Often such a reaction may be made to serve by resorting to the simple expedient of adding an excess of the titrant and then titrating back with another titrant that reacts with the first one. Acids and alkalies, and oxidants and reductants, are familiar examples of such companionate solutions. This procedure is never preferred to a direct titration, since it requires a second standard solution and thus brings in additional possibility of errors in measurement.

Examples of substances or situations that make a back titration desirable or necessary are as follows: (1) a volatile reactant, such as ammonia; (2) an insoluble substance, such as limestone; (3) an instable reactant, such as sulfite ion; (4) a slow reaction, such as that between trisulfatocerate and oxalate ions; and (5) lack of a suitable indicator, as encountered with bromine and certain types of organic compounds.

DETECTION OF EQUIVALENCE POINTS

As has already been stated, a usable titrimetric reaction implies the ability to determine readily that sufficient titrant has been used to complete the desired reaction. The place at which completion occurs is known as the *equivalence* or *stoichiometric* point of the titration. The *end point* of a titration is the place in the course of the titration where one actually stops, as in the titration of a base with an acid in the presence of an indicator compound, e.g., phenolphthalein. Ideally, this end point should coincide with the stoichiometric point.

[11] Usually analysts are happy if the degree of completion is within 1 part per 1000.

The titration of sodium hydroxide with hydrochloric acid involves the reaction

$$NaOH\ (40.01) + HCl\ (36.47) \rightarrow NaCl + H_2O$$

The reaction is complete when 40.01 g of sodium hydroxide has just reacted with 36.47 g of hydrogen chloride. The stoichiometric point marks the completion of this reaction.

In the majority of titrations the end point is merely a reproducible point that may be detected easily. Usually it is close to the stoichiometric point, and often any error may easily be compensated or evaluated. An example may be found in the next chapter for the titration of hydrochloric acid with sodium hydroxide, with methyl orange as the indicator. The analyst titrates to a *p*H near 4 rather than to a neutral solution of *p*H 7, which is the equivalence point if the solution is free of dissolved carbon dioxide. Standardizing and using the acid under the same conditions is an application of compensation of errors.

Since the success of a titration is intimately connected with the analyst's ability to obtain a given end point reproducibly, some of the means available for attaining this objective should be considered. In general, usable end-point processes involve a relatively rapid change in some easily followed property of the titration system. These properties involve changes in the titrant solution, the solution titrated, or some indicating substance added to the solution titrated. Only the general nature of the processes is summarized here, the details being reserved for subsequent chapters.

Change in Properties of the Titrated or Titrating System

One of the simplest procedures for determining the end point of titrations is to take advantage of some chemical reaction between the standard solution and the solution of the constituent being titrated. Several phenomena accompanying such reactions are employed as a means of marking the completion of titrations.

Change in color. If the color intensity, either of the standard solution or the constituent being titrated, is sufficient, this property may be used to mark the completion of titration. Two familiar examples may be cited. In the titration of the oxalate ion by permanganate, the end point is marked by the appearance of the purple hue resulting from a slight excess of titrant. Use of the disappearance of a color to mark an end point is illustrated in the titration of the triiodide ion I_3^- with thiosulfate, or of the ion $Cu(NH_3)_4^{++}$ with cyanide. In each case the titration is continued until the color just disappears.

Change in turbidity. In some systems certain turbidimetric phenomena serve to indicate the extent of reaction of the titrant with the constituent being titrated. Visual observation of the completion of precipitation may be so utilized, although the process is lengthy. With the titrant functioning as a precipitant, one would continue adding standard solution just to the point where no further precipitation takes place.

The appearance of a permanent precipitate may be used to indicate the end point, as in the reaction of cyanide ion with silver ion as the titrant. A precipitate appears when two moles of the former have reacted with one of the latter (see Chapter 15).

A method based upon the attainment of matched turbidities is employed in the Gay-Lussac process for determining silver by titration with sodium chloride. Incidentally, this method, proposed about 1830, is one of the earliest titrimetric processes, and it is still used in some mints to assay silver coinage.

Change in electrical properties. As titrations proceed, certain of the electrical properties of the solution undergo continuous change. The principles of some of these changes are presented in Chapter 18. At this point, it is sufficient to state that the change near the equivalence point is such that completion of the reaction can be determined by measurement of certain electrical properties.

Of the three common electrometric methods, potentiometric, conductometric, and amperometric, the first has been the more generally useful, alhough the last is finding increasing application at present. A new, fourth electrometric method, employing variations of high frequency oscillators, is proving useful in some cases.

The potentiometric method is based upon the determination of the potentials of suitable electrodes connected to a system being titrated. The end point usually is determined graphically from curves coordinating either the electrode potentials with the volume of titrating solution, or the change in potential per given amount of titrant.

In the conductometric method the electrical conductivity is measured as the titration proceeds. When these values are plotted against the amount of titrant used, a minimum or inflection in the curve will be found at the end point.

In the amperometric method [12] the current flowing on the application of a definite electrical potential to the electrode system is measured as

[12] It may be noted that this nomenclature is based upon the unit used in measuring the current, the ampere. It is an example of unfortunate naming, mentioned in Chapter 11. Other electrometric methods, such as potentiometric and conductometric, are not so named.

the titrant is added. In general, the appearance of the plotted titration data resembles the curves obtained in a conductometric titration.

Changes in other physical properties. Although the methods already mentioned are those most used in titrations without added indicator compounds, electrometric methods using other physical properties are also used. Following somewhat the procedure in electrometric methods in certain cases, one may determine, for example, temperature-volume or viscosity-volume curves for the titration. The end point is then determined in the same manner as with a conductometric titration.

It should be noted that the application of methods such as those described is merely a means for determining end points. The overall procedure is titrimetric measurement, since the amount of titrant used is the basis for calculating the amount of desired constituent.

Change in Properties of an Added Indicator Compound

In many titrations the completion of the process is marked by certain phenomena accompanying the reaction between an added indicator compound and either the titrant or a substance in the system being titrated. Such indicators show in several ways the attainment of end points.

Indicators may be used either internally or externally, although not all of them are applicable both ways. In the former use, the indicator is added to the solution to be titrated, generally before the titration is started, but occasionally just before the process is completed. The internal use of indicators is usually preferable.

In some instances the conditions in the reacting system are such that the indicator must be used externally. This practice is less common than formerly. To use the method, drops of the indicator solution are placed on some surface, such as a "spot" plate. At intervals during the titration, drops of the solution being titrated are removed and touched to the drops of indicator solution. This process is continued until the completion of the titration. To avoid undue tediousness, the analyst may take drops first in each 5 ml of titrant, then each 1 ml in the selected 5-ml interval, then each 0.1 ml in the selected 1-ml interval. The fourth and fifth titrations serve as the final checking determinations. Obviously, the method is to be avoided if possible.

Important phenomena used to indicate attainment of end points as a result of changes in added indicator compounds are summarized in the following sections.

Change in color. The color changes produced with indicator compounds often resemble those already mentioned. In this type of change, however, the variety of chemical reactions is greater than when the

titrant reacts with the solution titrated. Also the mechanism of the processes may differ markedly. Some of the principal kinds of reactions used will now be illustrated.

Completion of a reaction involving the appearance of a color is made evident through the formation of either a soluble species or a precipitated form sufficient to impart a color to the solution or to change the color of the solution or of a precipitate in it. The neutralization of an acid with a base in the presence of phenolphthalein illustrates the formation of a colored species. The use of potassium chromate as an indicator in the titration of the chloride ion with the silver ion depends upon the formation of reddish silver chromate at the end point.

In many cases there is a change from one color to another. This change may occur with either a soluble compound or a precipitate. The use of methyl orange in neutralization titrations illustrates change in a soluble compound, and a striking illustration of change in a precipitate occurs in titrations with certain adsorption indicators in precipitation reactions.

The following characteristics are desirable in an indicator compound: (1) an intense hue should be produced by a small amount of indicator compound, since a definite amount of the standard solution is needed to cause the color transformation; (2) the indicator should not be affected by possible side reactions; and (3) if possible, the change should be from a color to no color, or vice versa, rather than from one hue to another spectrally close to the first. Most individuals are most sensitive to color-no color changes.

Change in turbidity. Turbidimetric indications of end points are connected with the appearance or disappearance of precipitates at the completion of titrations. In the titration of the cyanide ion with silver ion in the presence of ammonium hydroxide, using iodide ion as an indicator, the first excess of titrant is marked by the appearance of an opalescence resulting from the formation of silver iodide. In contrast to this process, disappearance of the precipitate marks the end point in the titration of the ion $Ni(NH_3)_4^{+2}$ with cyanide ion, using silver iodide as the indicator. The first excess of cyanide ion forms the soluble ion $Ag(CN)_2^-$.

USE OF THE STANDARD SOLUTION

In the foregoing consideration of titrimetric methods, measurement of volume and the preparation of the titrant have been discussed. The third general topic of interest is the use of the standard solution.

Specific applications of different kinds of titrimetric methods are presented in subsequent chapters. Here only a brief summary is intended.

Titration Error

In many titrations the end point determined experimentally does not coincide exactly with the stoichiometric or equivalence point. The latter marks the point where exactly equivalent amounts of the solutions just react with each other. The difference between the end point and the equivalence point represents the titration error, or indicator blank.

From what has been stated regarding the reactions that take place between indicator compounds and solutions with which they are used, it may be inferred that an appreciable amount of titrant is often required to make the transformation evident, that is, the apparent amount of titrant is too large by the amount necessary to produce the end-point reaction.

Distinct from this possibility is another, different in nature. In titrating hydrochloric acid with sodium hydroxide, the analyst stops near *p*H 4 with methyl orange as the indicator, and near *p*H 8.5 with phenolphthalein as the indicator. The *p*H of the resulting sodium chloride is near 7, of course.

In accurate work the titration error may have to be taken into account. An empirical practice is to eliminate the error by compensation. For example, the solution of hydrochloric acid just mentioned may be used for titrating the sodium carbonate in soda ash. If the acid is standardized against sodium carbonate with methyl orange as the indicator, and then used for the soda ash under the same conditions, it makes no difference whether or not the end point used is the true equivalence point. Comparable volumes of titrant should be used, of course.

If determination of the magnitude of the error is desirable, one may measure directly the amount of titrant required to effect the desired color or other transformation. For example, a solution without any desired constituent is titrated as a blank. Correction may then be made for the blank so obtained.

Park[13] has suggested a method of calculation of error. If two or more samples of the same substance but of different weights are handled under the same conditions, the amount of excess reagent should be the same in each case. To illustrate the method, he cites the following data for the titration of a solution of zinc with ferrocyanide, using uranium nitrate as an outside indicator. Volumes of 10, 20, 30, and 40 ml of

[13] *Ind. Eng. Chem., Anal. Ed.* **8**, 32 (1936).

zinc solution required, respectively, 9.75, 19.13, 28.50, and 37.87 ml of ferrocyanide solution. Letting x equal the titration error, it is evident from these data that

$$
\begin{aligned}
28.50 - x &= 3(9.75 - x) && \text{and } x = 0.38 \\
28.50 - x &= 3/2(19.13 - x) && x = 0.40 \\
19.13 - x &= 2(9.75 - x) && x = 0.37 \\
37.87 - x &= 4(9.75 - x) && x = 0.38 \\
37.87 - x &= 4/3(28.50 - x) && x = 0.39 \\
37.87 - x &= 2(19.13 - x) && x = 0.39 \\
& && \text{Average } 0.38 \text{ ml}
\end{aligned}
$$

Applications

Reference to collections of standard methods of chemical analysis shows that many titrimetric procedures have been devised for a wide variety of industrial materials. Several monographs deal entirely with the theory and applications of such methods. The specific examples included in the three following chapters, together with the numerical problems and their applications in Chapter 33, are sufficient to show the broad utility of titrimetry.

Usually the outstanding general advantage of titrimetric methods is their speed, especially for large numbers of the same determination They are at their best in this respect when no separations are required to render the desired constituent susceptible to measurement. In the case of some determinations, however, the necessary separation(s) makes a single analysis, including the preparation of the titrant, longer than the equivalent gravimetric method.

Often, also, the skill required to make titrimetric measurements is less than that for certain other types of measurement. This has resulted in the practice in industrial laboratories of training technicians to perform one, or a few, particular kinds of determinations, day after day. Then the trained chemists of the laboratory are responsible for providing the standard solutions and seeing that the routine continues successfully.

The accuracy of many titrimetric methods is quite satisfactory, particularly if the most important sources of error, such as temperature changes, end point blanks, and other possibilities are taken into account. For exacting work each analytical method must be judged by itself, usually in terms of what can be done with a material of known composition. The sources of error should be understood and their probable magnitude determined. Compensation of errors by standardizing and using the titrant under comparable conditions is important.

CHAPTER 13

TITRIMETRY: NEUTRALIZATION METHODS

Titrimetric methods based upon neutralization reactions[1] include those in which the essential chemical process is the interaction of hydrogen and hydroxyl ions. From a practical standpoint, the following kinds of compounds can be determined in aqueous solution in this way: (1) acids and bases having sufficient degrees of ionization[2] (usually $> 10^{-8}$), such as hydrochloric and acetic acids and sodium and ammonium hydroxides; (2) salts of partially neutralized acids, such as potassium hydrogen sulfate and sodium dihydrogen phosphate; (3) salts of strong bases and weak acids, such as potassium carbonate and sodium borate; and (4) salts of strong acids and weak bases, such as hydrazine sulfate, $N_2H_4 \cdot H_2SO_4$.

Scope of Neutralimetry

Common examples of the titrimetric use of neutralization reactions are illustrated in the following equations, written in both molecular and ionic form:

$$HCl + NaOH \rightarrow NaCl + H_2O$$
$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$$

$$Ba(OH)_2 + 2\ HNO_3 \rightarrow Ba(NO_3)_2 + 2\ H_2O$$
$$Ba^{+2} + 2\ OH^- + 2\ H^+ + 2\ NO_3^- \rightarrow Ba^{+2} + 2\ NO_3^- + 2\ H_2O$$

$$KHSO_4 + KOH \rightarrow K_2SO_4 + H_2O$$
$$K^+ + H^+ + SO_4^{-2} + K^+ + OH^- \rightarrow 2\ K^+ + SO_4^{-2} + H_2O$$

$$Na_2CO_3 + H_2O \rightleftarrows NaOH + NaHCO_3{}^3$$
$$2\ NaOH + 2\ HCl \rightarrow 2\ NaCl + 2\ H_2O$$

[1] See Chapter 25 for laboratory exercises on neutralimetry.

[2] An electrolyte may be completely ionized, but the dissociation may be incomplete because of the presence of ion-pairs held together by covalent linkages. The terms "ionization" and "dissociation" are often used interchangeably.

[3] Sodium carbonate hydrolyzes enough to give a color with phenolphthalein. It is assumed, therefore, that the hydroxyl ions so formed are being titrated with the hydrochloric acid (last equation).

Examination of these equations shows that the fundamental reaction in all cases may be formulated as

$$H^+ + OH^- \rightarrow H_2O$$

Cations and anions other than hydrogen and hydroxyl ions appear on both sides of the equations. Neutralimetry may be defined, then, as the section of titrimetry that is based upon this reaction.

Rather generally, two subdivisions of neutralimetry are recognized: (1) *acidimetry,* in which the standard solution is an acid, by means of which alkaline substances are measured; and (2) *alkalimetry,*[4] in which the standard solution is a base, by means of which acidic substances are measured.[5] Examples of such applications are given in Chapter 25, and further possibilities are illustrated in the numerical problems in Chapter 33.

Acid-Base Nomenclature

After careful consideration, the Arrhenius definitions of acids, bases, and salts have been retained. An *acid* is a substance which dissociates a hydrogen ion or proton in aqueous solution; a *base* dissociates a hydroxyl ion. A *salt* is the product formed by the neutralization of such an acid with a base. Thus, solutions of hydrochloric acid HCl, and sodium hydroxide NaOH, react to give the salt sodium chloride, NaCl.

There can be no argument over the merits of the more generalized definitions of Brønsted and Lowry for acids and bases, as illustrated in the equations

$$\text{Acid} \rightleftarrows \text{base} + \text{proton}$$
$$\text{Acid}_1 + \text{base}_2 \rightleftarrows \text{acid}_2 + \text{base}_1$$

However, to abandon the conventional designations at this time would seem to involve difficulties in using the analytical literature comparable to those connected with a possible displacement of the normal system for specifying concentration of solutions.

If these newer definitions of acids and bases should be adopted, the term "neutralimetry" will be too limited. The term "protonimetry" would then be more adequate. It would include measurements in which the essential chemical process is a reaction between a proton and a base. The term "acidimetry" could be retained with substantially its present meaning, as used in this book; but the term "basimetry" should replace "alkalimetry." The general classification of titrimetric methods, in

[4] The term that seems to be co-ordinate with "acidimetry" is "basimetry." Thus far, however, it has not achieved acceptance.

[5] See Bell, *Acids and Bases: Their Quantitative Behavior,* Wiley, 1952.

terms of kinds of reactions involved, would need an overhauling. Thus, basimetry would require several subdivisions, since such reacting ions as hydroxyl OH^-, permanganate MnO_4^-, and chloride Cl^-, are bases according to Brønsted's ideas.

To use the terms "acid" and "base" in the sense adopted by G. N. Lewis involves even more difficulty, inasmuch as some substances function as either an acid or a base, depending upon the prevailing environment. This possibility has not been considered for purposes of analytical classification of methods.[6]

Equivalent Weights

If the normal system is used for designating the concentration of standard solutions, one must decide what fraction of a molecular weight of the acid or base solute is an equivalent weight.

In general, the analyst must know the chemical reaction involved, and from this, determine the number of hydrogen or hydroxyl ions *functioning* per molecule in the reaction. Then the equivalent weight of a substance undergoing a neutralization reaction is equal to the molecular weight of the substance divided by the number of hydrogen or hydroxyl ions with which the substance reacts. Some examples will illustrate this reasoning.

The equivalent weight of all monofunctional[7] acids or bases is equal to their molecular weight, since they react with or furnish 1 mole of hydrogen or hydroxyl ion, or their equivalent, per mole of compound. Polyfunctional compounds, that is, those providing more than one hydrogen or hydroxyl ion per molecule, are not so simple. In reactions illustrated by the equations

$$\mathbf{H_2SO_4} + 2\ NaOH \rightarrow Na_2SO_4 + 2\ H_2O$$
$$\mathbf{Ba(OH)_2} + H_2SO_4 \rightarrow BaSO_4 + 2\ H_2O$$
$$\mathbf{Na_2CO_3} + 2\ HCl \rightarrow 2\ NaCl + H_2O + CO_2\uparrow$$

one uses as the equivalent weights one-half the molecular weights indicated in boldface type.

However, if the reaction between sodium carbonate and hydrochloric acid is carried out near 0°, with phenolphthalein as the indicator, only 1 mole of acid reacts, as shown in the equation

[6] For a discussion of generalized acid-base theory, including the Brønsted-Lowry and the Lewis concepts, see the following: Alyea, *J. Chem. Educ.* **16,** 535 (1939); Kolthoff, *J. Phys. Chem.* **48,** 51 (1944); Luder and Zuffanti, *The Electronic Theory of Acids and Bases,* Wiley, 1946; Naiman, *J. Chem. Educ.* **25,** 454 (1948); Riddick, *Anal. Chem.* **24,** 41 (1952); and a group of papers in *J. Chem. Educ.* **17,** 124 (1940).

[7] The word "monoprotic" has been used in this sense. Older usage employed the terms "monobasic" and "monoacidic," respectively, for acids and bases.

$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$$

Then the equivalent weight of the sodium carbonate is the molecular weight.

With orthophosphoric acid H_3PO_4, the achievable equivalent weight is the molecular weight, or one-half the molecular weight, representing, respectively, the reaction of one or two of the hydrogen ions, as shown in the equations

$$H_3PO_4 + KOH \rightarrow KH_2PO_4 + H_2O$$
$$H_3PO_4 + 2\ KOH \rightarrow K_2HPO_4 + 2\ H_2O$$

It is impossible to detect the completion of the third neutralization stage of this acid in aqueous solution because of the hydrolysis of the tripotassium phosphate K_3PO_4 that would be produced.

THE COURSE OF NEUTRALIZATION REACTIONS

The course of a neutralization reaction, as the process proceeds in aqueous solution, can be understood best, perhaps, by considering the change which occurs in the hydrogen-ion concentration as the reaction takes place.

Concentration of hydrogen ions may be expressed in the conventional manner in moles per liter in solution, using the symbol $[H^+]$. The magnitude of the values encountered, especially in alkaline solutions, is often very small, e.g., 1.5×10^{-9}. Consequently, expressing them in a less cumbersome way is more convenient.

For this purpose Sørenson suggested the *p*H system. According to his notation, *p*H was defined as the *logarithm of the reciprocal of the hydrogen ion concentration.* Expressed in symbols, it is

$$\log \frac{1}{[H^+]} = pH = -\log [H^+]$$

Later developments have shown that, strictly speaking, *p*H cannot be defined in this way. A recent report[8] states that only an operational definition is defensible. This means that *p*H is a measured quantity, and that conditions of measurement determine what is obtained. What is really measured is the activity[9] of the hydrogen ion under specified

[8] Nat. Bur. Standards, Letter Circ. LC933, "Standardization of *p*H measurements made with the glass electrode"; see also Bates, *Electrometric* p*H Determinations: Theory and Practice,* Wiley, 1954.

[9] Activity, rather than concentration, is a measure of the active mass of a substance in solution. The following expression relates activity a and molar concentration c:

$$a = \gamma c$$

the activity coefficient of a particular constituent being represented by γ. The presence of other ions in the solution affects the magnitude of the activity coefficient. The value of γ ap-

TABLE 13.1

HYDROGEN ION CONCENTRATION OF VARIOUS SYSTEMS

State of Solution	$[H^+]$	*p*H	*Systems Included*
Acidic	$>10^{-7}$	<7	Solutions of acids, such as HCl. Solutions of acid salts, such as $KHSO_4$. Solutions of salts of strong acids and weak bases, such as NH_4Cl.
Neutral	10^{-7}	7	Liquids having equal activities for the hydrogen and hydroxyl ions, such as water. Solutions having approximately the same activities for the hydrogen and hydroxyl ions, such as an aqueous solution of a salt of an acid and a base having the same degrees of ionization.
Basic	$<10^{-7}$	>7	Solutions of bases, such as NaOH. Solutions of salts of strong bases and weak acids, such as Na_2CO_3 and $Na_4B_4O_7$.

conditions. Therefore,

$$pH = -\log a_{H^+}$$

In dilute solutions of hydrogen ions, concentration may be substituted for activities as a close approximation. This substitution has been made in the calculations in the following paragraphs.

We may now proceed with the subject of reactions in aqueous solutions. For the reaction represented by the equation

$$H_2O \rightleftarrows H^+ + OH^-$$

the dissociation constant for the water, K_w, is given by the expression,

$$K_w = [H^+] \times [OH^-]$$

The concentration of water in dilute or moderately concentrated solutions is constant, being 55.55 moles per liter at 25°. In general, the activity, and hence the effective concentration, of any condensed phase, liquid or solid, in contact with an aqueous solution is constant and may therefore be incorporated in the equilibrium constant.

The value of K_w is close to 10^{-14} at 22°. Then, for pure water, since

proaches unity in infinitely dilute solutions, where a finally equals c. In addition to increasing ionic concentrations, γ for a given ion is affected by other factors, such as valence of the ion, the specific nature of the ion, and the kind and concentration of other ions present. The detailed situation in any particular case is obviously one of some complexity.

$[H^+] = [OH^-]$,

$$[H^+] = \sqrt{10^{-14}} = 10^{-7} = [OH^-]$$

and the *p*H is 7.

On the basis of the mass law, one may predict that this ionic equilibrium for water will be affected by the addition of anything changing the concentration of the hydrogen or hydroxyl ions. Thus, the *p*H of 200 ml of water containing a few drops of concentrated sulfuric acid is much less than that for the water alone. A small amount of sodium hydroxide would produce the opposite effect, but in both cases one may speak of the hydrogen-ion concentration of the aqueous solutions, even though the value may be very low in the alkaline solution.

The *p*H of aqueous solutions varies over a wide range. Table 13.1 summarizes some information to indicate which are acidic, neutral, and basic.

Our next concern is what happens to the *p*H as acids and bases of different degrees of ionization are titrated with strong bases and acids, respectively.

Titration of a Highly Dissociated Acid

Hydrochloric acid may be taken as a typical strong, or highly dissociated, acid. If 100 ml of $M/10$ acid is titrated with $M/10$ sodium hydroxide, the progress of the neutralization will be accompanied by

TABLE 13.2

NEUTRALIZATION OF 100 ML OF $M/10$ HCl WITH $M/10$ NaOH

Per Cent Neutralization	*Molarity of Acid Remaining*	*Moles of H^+ per Liter*	$\frac{1}{[H^+]}$	*p*H
0.0	0.1000	0.1000	10.00	1.00
25.0	0.0600	0.0600	16.67	1.22
50.0	0.0333	0.0333	30.00	1.48
75.0	0.0143	0.0143	69.28	1.84
90.0	0.0053	0.0053	190.1	2.28
98.0	0.0010	0.0010	990.1	3.00
99.0	0.0005	0.0005	2000.0	3.30
99.9	0.00005	0.00005	20000.0	4.30
100.0	0.0000	10^{-7}	10^{7}	7.00
Per Cent Neutralization	*Molarity of Excess Base*	*Moles of OH^- per Liter*	$\frac{1}{[OH^-]}$	*p*H
100.1	0.00005	0.00005	20000.0	9.70
101.0	0.0005	0.0005	2000.0	10.70

a decrease in the amount of hydrogen ions remaining. The hydrogen-ion concentration will decrease steadily and the *p*H will increase. The calculated data in Table 13.2 indicate the direction and magnitude of these changes at different stages in the neutralization. All calculations are based on the assumption of complete dissociation and unit activity. Also, the molarities were calculated to take account of the dilution with addition of each increment of titrant.

Several points of interest in Table 13.2 should be noted. The initial *p*H of the acid is low and does not rise rapidly in the early stages of the neutralization. When the reaction is 90 per cent complete, the change is only 1.28 *p*H units. The last 5 per cent of the neutralization is notable because of the rapid rise in the *p*H. At the completion of the process it has reached a value of 7, which coincides with that for a solution containing sodium chloride in the amount formed by the reaction.

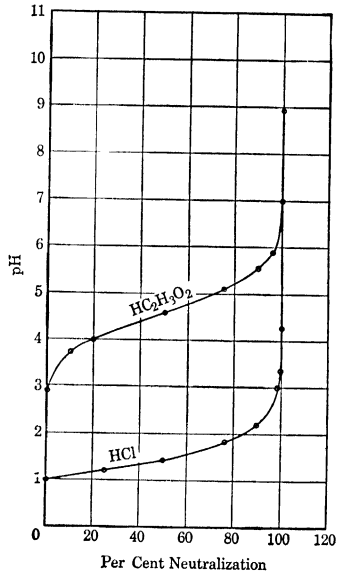


Figure 13.1

Course of neutralization.

It should be noted, too, that the reaction is essentially complete, that is, the acid is neutralized to within 1 part in a thousand when *p*H 4.3 is reached. In other words, the process is 99.9 per cent complete. For an excess of 1 part in a thousand of base, the *p*H reaches 9.7. Consequently, the reaction is analytically complete at any *p*H between 4.3 and 9.7.

In Figure 13.1 (HCl curve) are shown the *p*H data calculated for this titration. They are plotted with *p*H as the ordinate and per cent neutralization as the abscissa. Such a curve, determined experimentally, is known as a "potentiometric titration curve" (see Chapter 18 for explanation of such curves).

This curve is typical of those obtained in the reaction between strong acids and strong bases of the concentrations assumed for the calculations.

Titration of a Slightly Dissociated Acid

The titration of acetic acid with sodium hydroxide illustrates what happens when a relatively weak acid is neutralized with a strong base. The ionization constant of acetic acid is in the neighborhood of 10^{-5}.

The data for the titration of $M/10$ acid are shown in Table 13.3. The pH curve for this titration, also shown in Figure 13.1, exhibits several important contrasts with that for hydrochloric acid. First of all, the initial pH is higher. More significant yet is the relatively rapid rise of the curve during the first 10 per cent of the titration.

TABLE 13.3

NEUTRALIZATION OF 100 ML. OF M/10 $HC_2H_3O_2$ WITH M/10 NaOH

Per Cent Neutralization	*Molarity of Acid*	$[H^+]$	pH
0	0.100	1.33×10^{-3}	2.88
2	0.098	7.60×10^{-4}	3.12
5	0.095	4.00 "	3.40
10	0.090	2.05 "	3.69
20	0.080	9.10×10^{-5}	4.04
25	0.075	6.83 "	4.17
50	0.050	2.28 "	4.64
75	0.025	7.60×10^{-6}	5.12
90	0.010	2.53 "	5.60
95	0.005	1.20 "	5.92
100	0.000	1.34×10^{-9}	8.87

This rise may be interpreted in terms of the ionic equilibria involved. Before any base is added, we may consider the most important equilibrium to be represented by the equation

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

For the equilibrium expression

$$K_{HOAc} = \frac{[H^+] \times [OAc^-]}{[HOAc]}$$

the value of $K_{HOAc} = 1.85 \times 10^{-5}$ at 25°. The first portion of base added increases the concentration of the acetate ion OAc^-. This serves to decrease the concentration of hydrogen ion H^+, which gives rise to an increase in pH and an ascending curve.

As soon as appreciable amounts of acetate ions are formed, the solution exhibits what is known as buffer action.[10] Such systems are called buffer solutions, since in effect they have a capacity for resisting change in hydrogen-ion concentration upon the addition of acid or base to the solution. This amounts to their being able partially to maintain the status quo.

[10] The subject of buffers and their action is discussed in books on qualitative analysis.

The mechanism by which a solution containing a weak acid HA, and its salt with a strong base, BA, maintains its *p*H relatively constant against additions of small amounts of acids or bases involves the reactions represented by the equations

$$HA \rightleftarrows H^+ + A^-$$

$$BA \leftrightarrows B^+ + A^-$$

On addition of an acid,

$$H^+ + A^- \rightarrow HA$$

or a base,

$$OH^- + HA \rightarrow H_2O + A^-$$

By such reactions the effect of added acid or base is neutralized. The buffering action reaches its maximum capacity when equal amounts of acid and its salt are present.

Referring to Figure 13.1 again, the *p*H curve for acetic acid does not reach the line of equivalent amounts (100 per cent neutralization) until above *p*H 6. The actual point of completion of reaction lies close to *p*H 9, which is distinctly on the basic side of neutrality. This *p*H represents, of course, the value for a solution of sodium acetate having the same concentration as the reaction system at the end of the titration.

Attention has been directed to the fact that the data for the *p*H curves just discussed were calculated for assumed degrees of dissociation for hydrochloric acid. The values for acetic acid are experimental. The curves shown later were experimentally determined. Consequently, in these cases the *p*H values are actually based on activities rather than calculated values.

Calculation of pH at the Equivalence Point

The *p*H at the equivalence point can be calculated if the reaction goes to completion. On the basis of this calculation, one of the indicators discussed later can be selected for the titration.

In the titration of a highly dissociated base with a similarly dissociated acid, and in the reverse titration, the *p*H range encompassing the equivalence point is determined by the concentration of the solution. It is approximately *p*H 3 to 11 for 1 *N* solutions, *p*H 4 to 10 for 0.1 *N* solutions in the absence of carbon dioxide,[11] and *p*H 5 to 9 for 0.01 *N* solutions at the boiling point. This is shown by the nearly vertical portion of the curves in Figure 13.6.

If one of the reactants is slightly dissociated while the other is highly dissociated, the equivalence point *p*H can be calculated on the basis of

[11] The *p*H of water saturated with carbon dioxide is about 5.2 at room temperatures.

the equilibria involved. Thus, in the titration of a slightly dissociated acid HA, such as acetic acid, with a strong base, such as sodium hydroxide, the following equilibria prevail at the equivalence point:

$$\begin{aligned} NaA &\rightleftarrows Na^+ + A^- \\ A^- + H_2O &\rightleftarrows HA + OH^- \\ H_2O &\rightleftarrows H^+ + OH^- \end{aligned}$$

The equilibrium constant for the second reaction, which represents the hydrolysis of the salt formed in the reaction, is

$$K_{\text{Hyd}} = \frac{[HA] \times [OH^-]}{[A^-]} = \frac{[HA] \times [OH^-] \times [H^+]}{[A^-] \times [H^+]} = \frac{K_w}{K_a}$$

where K_a is the dissociation constant of the weak acid and K_w is the ion product constant for water. Since the concentrations of undissociated HA and of hydroxyl ion are effectively the same at the equivalence point, we may write,

$$\frac{K_w}{K_a} = \frac{[OH^-]^2}{[A^-]} = \frac{K_w^2}{c[H^+]^2}$$

where c is the concentration of the salt NaA, formed at the equivalence point. By rearrangement,

$$[H^+]_{\text{eq.pt.}} = \sqrt{\frac{K_w K_a}{c}}$$

or, by taking the —log of the expression,

$$p\text{H}_{\text{eq.pt.}} = \tfrac{1}{2} (pK_w + pK_a + \log c)$$

For the common weak acids and the usual concentrations used, the pH at the equivalence point will be about 8 to 10.

Similarly, the titration of a slightly dissociated base BOH, with a strong acid, such as hydrochloric, can be considered. The equilibria at the equivalence point are

$$\begin{aligned} BCl &\rightarrow B^+ + Cl^- \\ B^+ + H_2O &\rightleftarrows BOH + H^+ \\ H_2O &\rightleftarrows H^+ + OH \end{aligned}$$

For the hydrolysis of the salt formed,

$$K_{\text{Hyd}} = \frac{[BOH] \times [H^+]}{[B^+]} = \frac{K_w}{K_b}$$

where K_b is the dissociation constant of the weak base, BOH. Further treatment of the data, since $[BOH] = [H^+]$, yields

$$\frac{K_w}{K_b} = \frac{[H^+]^2}{[B^+]} = \frac{[H^+]^2}{c}$$

and, on rearranging,

$$[H^+]_{eq.pt.} = \sqrt{\frac{c\,K_w}{K_b}}$$

or

$$pH_{eq.pt.} = \tfrac{1}{2}\,(pK_w - pK_b - \log c)$$

The equivalence pH for titratable weak bases, such as ammonium hydroxide, at the usual concentrations, will be between 4 and 6.

In the remaining possible case, the titration of a slightly dissociated acid with a slightly dissociated base, the pH change near the equivalence point is very gradual. Since the analyst may select a highly dissociated titrant, there is no practical need to make such a titration.

DETERMINATION OF EQUIVALENCE POINTS

In actual titrations the analyst has the important problem of determining when the reaction has been brought to completion; that is, he must measure, to within one part in a thousand, the amount of standard solution that is equivalent to the constituent being determined.

What is achieved practically, of course, is an end point in the titration. In neutralization reactions most frequently use is made of the methods which involve application of electrometric titrations, or of indicator compounds added to the system titrated. Two of these possibilities are discussed.

Potentiometric End Points

Of the common electrometric methods, potentiometry has been the most useful. Chapter 18 contains a brief discussion of the theory of

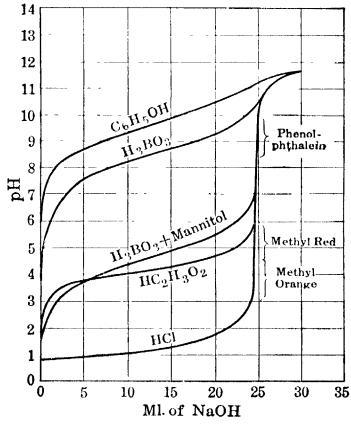


Figure 13.2

Neutralization curves for acids.

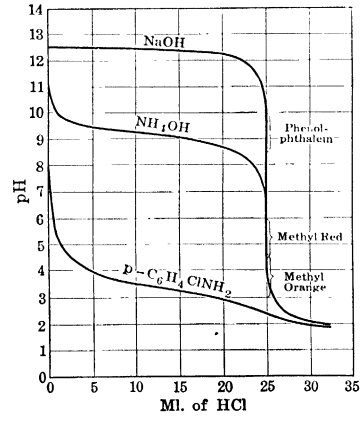


Figure 13.3

Neutralization curves for bases.

the determination of potentiometric titration curves. Reference should be made, therefore, to this material, as well as to other electrometric methods described there.

Monofunctional compounds. Figures 13.2 and 13.3 show potentiometric titration curves for a number of solutions of acids and bases. The acids and bases are represented by compounds with degrees of dissociation that may be considered as practically complete, relatively small (10^{-5}), and very small ($<10^{-8}$). Table 13.4 lists comparable substances in each group.

TABLE 13.4

ACIDS AND BASES OF DIFFERENT DEGREES OF DISSOCIATION

Compound	*Ionization Constant K at 25°*	*pK*
Strong acids		
Hydrochloric		
Nitric		
Perchloric		
Phosphoric, 1st H	7.54×10^{-3}	2.12
Sulfuric, 2d H	1.20×10^{-2}	1.92
Chloroacetic	1.38×10^{-3}	2.85
Oxalic, 1st H	5.01×10^{-2}	1.30
Phthalic, 1st H	1.29×10^{-3}	2.89
Weak acids		
Acetic	1.75×10^{-5}	4.75
Benzoic	6.32×10^{-5}	4.20
Hydrofluoric	1.70×10^{-5}	4.80
Phosphoric, 2d H	6.23×10^{-8}	7.20
Very weak acids		
Boric	5.80×10^{-10}	9.24
Hydrocyanic	7.25×10^{-10}	9.14
Phenol	1.20×10^{-10}	9.92
Phosphoric, 3d H	4.79×10^{-13}	12.32
Strong bases		
Alkali metal hydroxides		
Alkaline earth metal hydroxides		
Weak bases		
Ammonia	1.75×10^{-5}	4.76
Dimethylamine	8.92×10^{-4}	3.05
Methylamine	3.62×10^{-4}	3.44
Trimethylamine	6.15×10^{-5}	4.21
Very weak bases		
Aniline	2.68×10^{-10}	9.57
Hydroxylamine	6.60×10^{-9}	8.18
Pyridine	1.07×10^{-9}	8.97

The potentiometric procedure usually consists in using the experimentally determined *p*H values to draw the curves as shown, and then of determining the end points by inspection of the graphs. It will be noted in Figure 13.2 that there is a relatively steep portion in all the curves except for the slightly dissociated compounds, that is, boric acid, H_3BO_3, and phenol, C_6H_5OH.

The amount of titrant required to reach the end point is determined by locating the mid-point of the steep portion, or rise, of the curve and then dropping a line perpendicularly from this point to the base line. Whenever the rise in the curve is relatively sharp and has a steep portion of reasonable length, this procedure is quite satisfactory. In general, this conclusion is valid for compounds having dissociation constants larger than 10^{-5}. For curves such as that shown for boric acid, there is more uncertainty in selecting the right point in the rise of the curve, and, consequently, less reliability in the measurement. For compounds such as phenol, C_6H_5OH, the method is of little value.

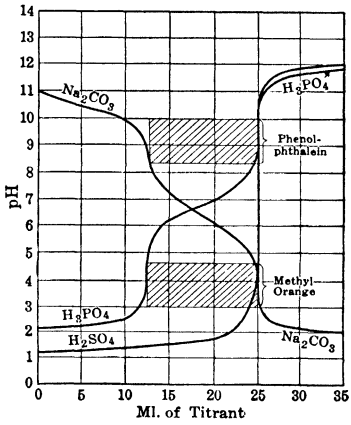


Figure 13.4

Neutralization curves for polyfunctional compounds.

Although the curve for boric acid alone is unsatisfactory for locating an end point closely, the rise can be much improved by taking advantage of an interesting bit of chemistry. This acid acts as if it had a considerably higher degree of dissociation if certain polyhydroxy organic compounds, such as glycerol or mannitol, are added to the system. The organic molecule must contain a sufficient number of hydroxyl groups and they must be properly oriented to give the effect. One curve in Figure 13.2 shows what happens when mannitol is present.[12]

In contrast to the above method of plotting the data, another procedure has some advantage. This procedure consists in using the *change* in the *p*H (or potential *E*) per unit volume of titrant as the ordinate, as described in Chapter 18.

Polyfunctional compounds. The discussion of *p*H curves has been confined thus far to acids and bases yielding, respectively, one hydrogen

[12] For a discussion of the boric acid-polyhydroxy compound reaction, see Hollander and Rieman, *Ind. Eng. Chem., Anal. Ed.* **17**, 602 (1945), and Schäfer, *Z. anorg. allgem. Chem.* **247**, 96 (1941).

or hydroxyl ion per molecule. In Figure 13.4 are shown curves for $M/10$ solutions of sulfuric and orthophosphoric acids, and sodium carbonate titrated with $M/10$ sodium hydroxide and hydrochloric acid, respectively.

The curve for sulfuric acid resembles closely that for hydrochloric acid, as shown in Figure 13.2. There is no significant evidence of a rise at the point of neutralization of the first hydrogen titrated. This fact indicates that the two equilibrium constants for the dissociation processes are relatively close together.

The curve for phosphoric acid shows a very different result. When one equivalent of base has reacted, there is a sharp rise in the region where methyl orange shows an end point. Practically, this titration is recommended for the determination of the acid. When more base is added, another rise occurs, this time where two equivalents have reacted. Phenolphthalein may be used to detect this end point. Still further addition of base causes some rise in the curve where the third hydrogen should react, but the change in direction of the curve is too gradual to be useful for a good end point. For this compound the values of the three equilibrium constants are 7.5×10^{-3}, 6.2×10^{-8}, and 4.8×10^{-13}.

In general, a polyfunctional compound will show separate rises (drops) in the pH titration curve if the equilibrium constants for the different stages of dissociation differ by about 10^4. The same is true for a mixture of weak and strong acids of comparable concentration.[13]

A few basic compounds show intermediate steps in their pH titration curves, the most familiar example being sodium carbonate. In this case, to have the intermediate portion of the curve well marked, it is necessary to titrate in such a way that the reaction will proceed as nearly as possible according to the equation

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

or, ionically

$$CO_3^{-2} + H^+ \rightarrow HCO_3^-$$

Since there must be no loss of carbon dioxide according to this reaction, the solution being titrated is kept near 0°, and the acid is added slowly to avoid local excess. Even so, the first drop in the curve is not as good as the first rise in the curve for phosphoric acid. However, an end point is obtainable with phenolphthalein as the indicator. In part, the lack of rapid change may be attributed to the fact that a buffer system involving sodium hydrogen carbonate has been synthesized.

[13] For a mathematical treatment of the problem of titrating mixed acids, see Mysels, *J. Chem. Educ.* **18**, 478 (1941).

The second drop in this curve is quite satisfactory and methyl orange serves as the indicator. On adding methyl orange first to a solution of sodium carbonate and titrating, the analyst goes directly to the second end point. This is the titration system recommended later (Chapter 25) for the standardization of a solution of hydrochloric acid. Phenolphthalein can also be used as the indicator for the complete titration, if the solution is kept near the boiling temperature to eliminate carbon dioxide.

End Points Using Indicator Compounds

For neutralization reactions, the three organic compounds, methyl orange, methyl red, and phenolphthalein, are probably the three most commonly used internal indicators. They are typical, in various ways, of several hundred similar substances.

Since so many of these compounds are usable for neutralization titrations, external indicator compounds of this kind are not necessary.

In general, neutralization indicators are very weak acids or bases. If an indicator is represented as a weak acid having the formula HIn, the mechanism of ionization may be represented as,

$$HIn \rightleftarrows H^+ + In^-$$

Application of the mass law gives

$$K_{HIn} = \frac{[H^+] \times [In^-]}{[HIn]}$$

On rearranging,

$$[H^+] = K_{HIn} \frac{[HIn]}{[In^-]}$$

If one color (hue) is attributed to the unionized molecule, HIn, and another to the indicator anion, In^-, the two colored forms[14] are present in equal concentration when the hydrogen-ion concentration is equal to the value of the ionization constant, that is, when $[H^+] = K_{HIn}$. From this viewpoint the ionization constant becomes the most notable property of the indicator, in that it determines where on the *p*H scale this midway transformation point comes.

Of course, the indicator may not exhibit its half-way color at this point, since with two-colored indicators one hue may be more intense (in equal concentration) than the other. Therefore, the useful part of the transformation range, in which the solution of the indicator exhibits a change of color, is confined to that part in which the less intense form is in excess. The hue of methyl red, for example, is quite reddish-purple below *p*H 5

[14] One of the forms may be colorless.

and only somewhat yellowish above this pH, which marks about the 50-per cent transformation point.

The color change of indicators may be interpreted from a slightly different viewpoint. If α represents the fraction of the indicator compound present in the form showing the color produced by a base, and $1 - \alpha$ represents the fraction in the form showing the color produced by an acid, one may write

$$[H^+] = K_{HIn}\left(\frac{1 - \alpha}{\alpha}\right)$$

and

$$\log [H^+] = \log K_{HIn} = \log\left(\frac{1 - \alpha}{\alpha}\right)$$

Then,

$$p\text{H} = pK_{HIn} + \log\left(\frac{1 - \alpha}{\alpha}\right)$$

The data in Table 13.5 have been calculated for methyl red, the pK of

TABLE 13.5

THE RELATION BETWEEN pH AND α

α	$1 - \alpha$	$\log \alpha$	$\log (1 - \alpha)$	$\log \frac{\alpha}{(1 - \alpha)}$	pH
0.1	0.9	0	0.954	−0.954	4.05
0.15	0.85	0.176	0.929	−0.753	4.25
0.2	0.8	0.301	0.903	−0.602	4.4
0.3	0.7	0.477	0.845	−0.368	4.6
0.4	0.6	0.602	0.778	−0.176	4.8
0.5	0.5	0.699	0.699	0.000	5.0
0.6	0.4	0.778	0.602	+0.176	5.2
0.7	0.3	0.845	0.477	+0.368	5.4
0.8	0.2	0.903	0.301	+0.602	5.6
0.85	0.15	0.929	0.176	+0.753	5.75
0.9	0.1	0.954	0.000	+0.954	5.95

which is close to 5. They illustrate how the fraction present in the basic form varies with the pH of the system.

Between the limits $\alpha = 0.2$ and $\alpha = 0.8$, a change of 10 per cent, or 0.1 in the fraction, corresponds to a variation of about 0.2 pH unit. At either extreme the variation is much different, being about 0.35 unit from $\alpha = 0.8$ to $\alpha = 0.9$. To make $\alpha = 100$ per cent, the pH would have to be infinite, as the above equation shows. Consequently, no finite value of pH would make α equal to 100 or 0 per cent.

If α is plotted against pH, the curve shown in Figure 13.5 is obtained.

The ends never reach 100 nor zero per cent. The value of α controls primarily the hue of the solution containing the indicator. From 0.9 to 0.99 the hue changes little, although the pH rises from 5.95 to 6.99. The useful range of the indicator lies in the general region between 10 and 90 per cent transformation. For many indicators this is about 1.6 pH units. The shaded portion of the curve represents the transformation region in which a small change in pH effects the greatest hue change.

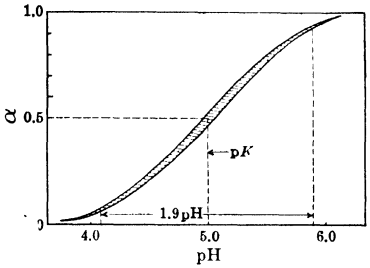


Figure 13.5

Fraction α of indicator transformed.

The curve shown is similar to those for many other indicators. The chief difference is the lateral displacement because of different pH ranges. When $pK = p\text{H}$ the curves all cut the horizontal line where $\alpha = 0.5$. A set of buffer solutions is very useful for demonstrating the actual hues exhibited by different indicators at different pH values, and for demonstrating also where in the pH scale the hue transformation occurs. There are many one- and two-, and some three-color indicators, and a variety of hues. In every case the change from one hue to another requires a certain pH range; it never occurs at a point.

TABLE 13.6

COLOR CHANGE AND pH RANGE OF SELECTED INDICATORS

	pH													
Indicator	0	1	2	3	4	5	6	7	8	9	10	11	12	13
Thymol blue	R*	R ⟷	Y	Y	Y	Y	Y	⟷	B	B	B	B		
Brom phenol blue	Y	Y	Y	⟷	B	B	B	B	B	B	B	B		
Methyl orange	R	R	R	⟷	Y	Y	Y	Y	Y	Y	Y	Y		
Brom cresol green	Y	Y	Y	Y	⟷	B	B	B	B	B	B	B		
Methyl red	R	R	R	R	R ⟷		Y	Y	Y	Y	Y	Y		
Chlor phenol red	Y	Y	Y	Y	Y	Y ⟷	R	R	R	R	R	R		
Brom thymol blue	Y	Y	Y	Y	Y	Y	⟷	B	B	B	B	B		
Phenol red	Y	Y	Y	Y	Y	Y	Y ⟷	R	R	R	R	R		
α-Naphtholphthalein	Y	Y	Y	Y	Y	Y	Y	Y	⟷	B	B	B		
Phenolphthalein	C	C	C	C	C	C	C	C	C ⟷	R	R	R		
Thymolphthalein	C	C	C	C	C	C	C	C	C	C ⟷	R	B		
	0	1	2	3	4	5	6	7	8	9	10	11	12	13

* R = red (reddish-purple); B = blue; Y = yellow; C = colorless.

Table 13.6 lists a few of these indicators, together with their color-transformation ranges and hue changes.

Selection of Indicators

As previously stated, the most important problem is the selection of a suitable indicator for a given titration. As a general conclusion, titrations can be accomplished with a reasonable degree of precision only for those systems yielding *p*H curves with a relatively steep rise. Then, to be suitable for the titration, an indicator must at least meet the requirement of having its *p*H range lie within a portion of the steep part of the curve. The basis for this conclusion will now be examined.

When only a small amount of titrant, that is, a drop or two of the solution is required to bring about the desired color transformation in the indicator, the end point is said to be sharp. For this to happen, the small amount of titrant must change the *p*H of the solution enough to effect a visible change of color.

There are several methods for choosing a suitable indicator. (1) The *p*H of the solution at the equivalence point can be calculated and an indicator selected the pK_a of which equals the computed *p*H. (2) A solution can be prepared that is identical in composition with that which should exist at the equivalence point. Then the *p*H of this solution can be determined and an indicator selected the range of color change of which has this *p*H at its mid-point. (3) Various possible indicators can be added to different portions of the equivalence point solution described, and a drop of acid or base, depending upon the titrant used, can then be added to each portion. The indicator found to give the greatest color change is preferable.

Figure 13.2 shows that the steep portion of the curves for $M/10$ solutions of strong acids and bases extends from *p*H 4 to *p*H 10. A considerable number of indicators have their transformation ranges within these limits and can, therefore, be used. Methyl orange and phenolphthalein represent the outside limits usually employed. For the titration of relatively weak acids or bases, such as acetic acid or ammonia, respectively, the choice is more restricted. The respective *p*H ranges are approximately 7 to 10 and 4 to 7.

The titration of acetic acid, with methyl orange as indicator, illustrates what happens if an indicator, the *p*H range of which does not lie opposite the steep portion of the curve, is used. The curve in Figure 13.2 reveals that the end point in such a case would come far too soon and that only about a third of the total base that should be required for neutralization

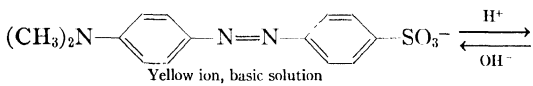
would be sufficient to effect the color change. Furthermore, the color transformation would be very gradual.

This same effect of gradual color change is encountered in the attempt to titrate any compound having an ionization constant of the order of that of boric acid (10^{-9}), even though the *p*H range of the indicator lies opposite the rise in the curve. If one has no alternative, approximate determinations can be made by titrating to the color of a solution prepared to have the *p*H of the point where the curve crosses the line of equivalent amounts. In Figure 13.2 this would be about 10.3 for boric acid. The standard prepared should coincide as nearly as possible with the solution titrated in such items as concentration of indicator, volume of solution, vessel used, and concentration of the product formed.

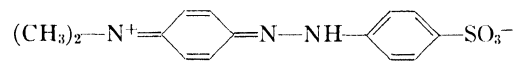
Commonly Used Indicators

Only brief reference can be made here to a few acid-base indicators very commonly used in titrations. A few others are mentioned in Table 13.5. Such compounds are referred to again in Chapter 29 for use in the colorimetric determination of *p*H. Reference works should be consulted for further information concerning these compounds.[15]

Methyl orange. Methyl orange, discovered in 1878 by Lunge, has been widely used in titrations. It is the sodium salt of paradimethylaminoazobenzenesulfonic acid. Its formula in acidic and basic solution may be represented as follows:



Yellow ion, basic solution



Purplish-red ion, acidic solution

The simple equilibrium postulated on page 209 is too limited to account for all the facts. There is convincing evidence that molecular rearrangements occur that involve the chromophoric or color-forming groups as the equilibrium shifts with changes in the *p*H of the solution. The purplish-red hue is attributed to the quinoid group $=C_6H_4=$, which predominates in acidic solution; the yellow hue is attributed to the azo group $-N=N-$, which predominates in basic solutions. Most of this change occurs within the usable *p*H range of 3.0 to 4.6 (compare Figure 13.5).

[15] Kolthoff and Rosenblum, *Acid-Base Indicators,* Macmillan, 1937; Kolthoff and Laitinen, *pH and Electrotitrations,* Wiley, 1941.

An aqueous solution containing 1 g per liter of methyl orange is suitable for titrimetry. In ordinary titrations the use of more than two drops of this solution in a 50-ml sample solution makes the point of color change somewhat indefinite.

Modified methyl orange. For most purposes, many workers prefer a modified solution of methyl orange.[16] It is prepared by dissolving 2 g of methyl orange in 500 ml of water, and 2.8 g of xylene cyanole FF in 500

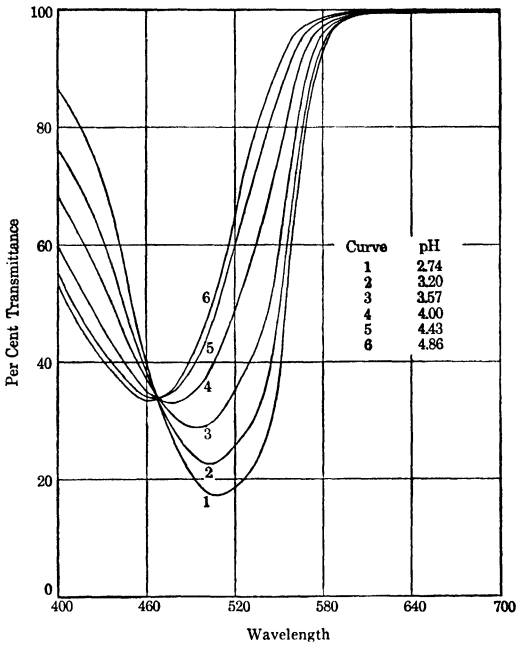


Figure 13.6

Spectral transmission curves for methyl orange solutions at different *p*H values.

ml of 95-per cent ethanol, and then mixing the two solutions. Its color change is from green in alkaline solutions to magenta in acidic solutions.[17] If a small amount, preferably one drop, of this solution is used, and if the titration is performed slowly near the end point, one can obtain a solution which is practically colorless for the completion of the titration. Some analysts prefer such a transformation, that is, from a hue to no hue (or the reverse), rather than from one hue to another.

Since the *p*H range of the modified solution is the same as that for methyl orange alone, the mixture can be substituted wherever methyl orange is specified for titrations. The *p*H of the colorless portion of the

[16] Hickman and Linstead, *J. Chem. Soc.* **121**, 2502 (1922).

[17] A student who is color-blind to the changes of methyl orange can use this mixture.

transformation range is approximately 3.8 to 4.0. Figures 13.6 and 13.7 show the effect of the xylene cyanole FF on the absorption spectrum of methyl orange solution at different *p*H values. Such curves are explained in Chapter 17.

This modified solution should not be used in the presence of strong oxidants, such as bromine water. Apparently, in such cases the methyl orange is oxidized, and its color destroyed, and only the modifier, which has no *p*H-indicating property is left.

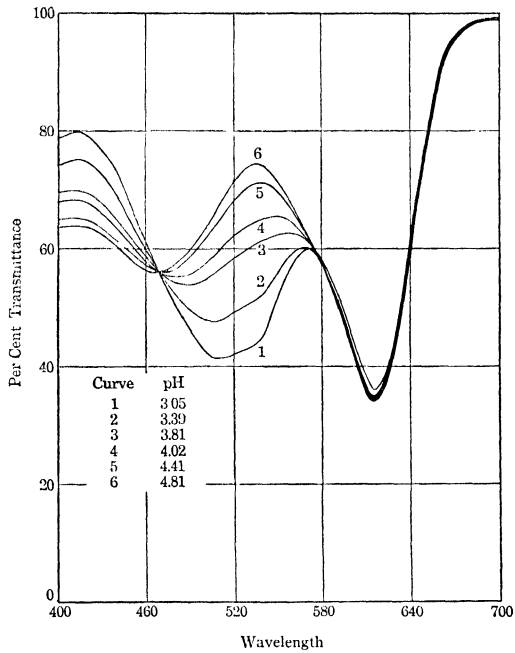


Figure 13.7

Spectral transmission curves for modified methyl orange at different *p*H values.

Methyl red. Methyl red differs from methyl orange in that it contains an *ortho*-carboxylic acid group (-COOH) rather than a *para*-sulfonic acid group ($-SO_3H$). Because of this change in structure, the *p*H range of methyl red is shifted to 4.4 to 6.0, compared to 3.0 to 4.6 for methyl orange. This difference in range illustrates one effect resulting from changing functional groups, and their position, in such compounds.

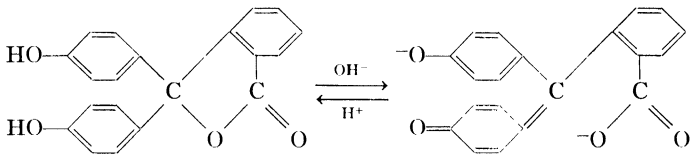
The hues of the basic and acidic forms are similar to the respective hues for methyl orange. The colors of methyl red are slightly more intense than those for methyl orange, and the *p*H range is a little better located with respect to the steep portion of the titration curves of many solutions.

The latter characteristic results in sharper end points. Probably because of these properties, methyl red is preferred by many people.

A 0.1 per cent solution in 95 per cent ethanol serves for titrations. A modified solution may be made by dissolving 1.25 g of methyl red and 0.83 g of methylene blue in enough 90 per cent ethanol to make 1 liter.[18]

Phenolphthalein. Phenolphthalein is a one-color indicator, the form in acids being colorless and that in bases (not too concentrated) being purplish-red.

The equilibrium forms for phenolphthalein may be represented by the formulas,



Colorless acidic solution — Purplish-red basic solution

The one chromophoric group $=C_6H_4=$, appears only in the basic form. In very alkaline solution this group is destroyed, with the formation of a different colorless structure.

A 0.5 per cent solution in 95 per cent ethanol is suitable for titrations. A solution in 60 per cent Cellosolve is said to evaporate less rapidly than the ethanolic solution. The *p*H range is 8.3 to 10.0.

Mixed indicators. For some titrations, various people prefer a mixture of indicators, usually no more than two. An example is a mixture of methyl red and brom cresol green for the titration of ammonia.[19]

Mixtures known as "universal indicators" are mentioned in the discussion of colorimetry (Chapter 17).

FACTORS AFFECTING END POINTS[20]

A number of practical factors affect the reliability of end points. Several of the most important are considered briefly.

Concentration of Solutions Titrated

It is of interest to compare the *p*H titration curves for $M/10$ and $M/1$ solutions of hydrochloric acid titrated with a base of similar concentration. Simple calculations show that changing the concentrations of the reactants serves only to change the *p*H of the system. Although a $M/1$

[18] Johnson and Green, *Ind. Eng. Chem., Anal. Ed.* **2,** 2 (1930).

[19] Pieters, *Chem. Weekblad* **32,** 539 (1935); Ma and Zuazaga, *Ind. Eng. Chem., Anal. Ed.* **14,** 280 (1942).

[20] See Eastman, *J. Am. Chem. Soc.* **47,** 332 (1925); **50,** 418 (1928); **56,** 2649 (1934); and Roller, *J. Am. Chem. Soc.* **50,** 1 (1928); **54,** 3485 (1932) for mathematical treatment of error in acid-base titrations.

solution is not quite as highly dissociated as one one-tenth as concentrated, the actual amount of hydrogen ions present is greater, and the *p*H is lower. Figure 13.8 shows that the length of the steep portion of the curve is directly proportional to the concentration of the reactants. This part of the curve may be shortened so much that an indicator suitable for a 0.1 *M* solution will not be satisfactory for a 0 01 *M* solution. Thus, methyl orange is known to be unsatisfactory for very dilute solutions.

Also, the solutions reacting may be so dilute that the indicator color change is difficult to detect because of the small effect produced by each drop of titrant.

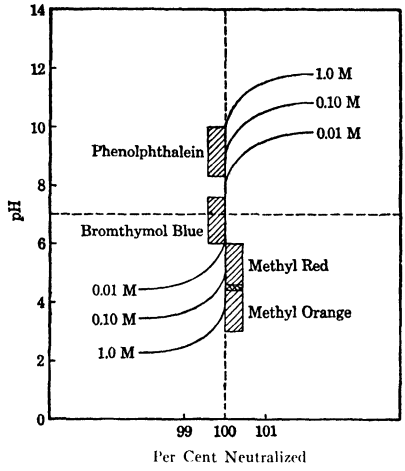


Figure 13.8

Effect of concentration on the length of the vertical portion of the curve.

Concentration of Indicator

A practical question in titration concerns the amount of indicator solution to use in a given titration for the optimum results, that is, to obtain the most evident color change with the use of the least amount of titrant possible.

Although no general recommendation can be made for every specific case, certain generalizations as to concentration of indicator are possible. If insufficient indicator is present, the color intensity is too low for the color change to be easily observable. Likewise, too much indicator makes the color change equally difficult to detect because the intensity is too deep. In the latter case, too, an appreciable amount of titrant is required to effect the color transformation.

In general, the analyst uses the smallest amount of indicator that will give a readily apparent color change in the system concerned. One or two drops, for the solutions of methyl orange, methyl red, and phenolphthalein previously described, added to 50 ml of solution, are usually satisfactory.

Direction of Titration

In many academic laboratories, it is a common practice to have students determine the ratio of equivalent volumes of solutions of an acid and

of a base. Does it make any difference whether the acid is titrated with the base, or vice versa?

To answer this question, let us turn again to Figures 13.2 and 13.3 to examine the curves for the HCl vs. NaOH and the NaOH vs. HCl titrations. Assume that methyl orange is the indicator. On titrating acid with base and stopping at *p*H 4, one would add not quite enough base to reach the neutral point of *p*H 7. The ratio of volume of acid to volume of base is slightly greater than 1 for equimolar solutions. If the order of titration is reversed, enough acid will be added to pass through *p*H 7 to reach the end point at *p*H 4. Again the ratio of acid to base is greater than 1. However, careful experimental determination of these ratios may demonstrate a small difference. A psychological factor is involved, since the end point is being approached with different changes in color, one being from the reddish-purple to yellow and the other being the reverse.

End-Point Error

The approximate amount of acid required to bring the solution from *p*H 7 to 4 (or the reverse) can be computed. Assuming a sample volume at the end point of 100 ml and the use of 0.1 *N* acid, the excess required, ΔV, is calculated as follows:

$$\Delta V = \frac{\text{milliequivalents of } H^+ \text{ needed}}{\text{milliequivalents of } H^+ \text{ per ml of acid used}}$$

$$= \frac{\text{meqs. of } H^+ \text{ needed}}{N \text{ of acid}}$$

$$= \frac{100\,(10^{-4} - 10^{-7})}{0.1}$$

$$= 0.10 \text{ ml}$$

This evidence brings out an important point, already mentioned, namely, that one seldom stops any acid-base titration at the neutral point. The solution is not neutral when equivalent amounts of acid and base have reacted, unless both solutes are equally ionized. With brom thymol blue, having a transition range of 6.0 to 7.6, the end point, of course, should be close to *p*H 7. In the cases of the two most commonly used indicators, methyl orange and phenolphthalein, the end points observed appear near *p*H 4 and 9, respectively.

Even though such points are not at *p*H 7, any error involved in a specific case may be compensated by standardizing and using the titrant under the same conditions. The indicator merely provides a reproducible point to which both titrations can be brought.

Standardization with Different Indicators

It is interesting to determine the molarity of a solution of sodium hydroxide by titrating a solution of acid, using several indicators of different *p*H ranges, such as methyl orange (3.0 to 4.6), methyl red (4.4 to 6.0) and phenolphthalein (8.3 to 10.0). A different molarity is obtained with each of these indicators, as might be predicted from inspection of Figure 13.2.

In the titration of hydrochloric acid with sodium hydroxide, the color change of methyl orange is reached first. Slightly more base solution is required to reach the color change of methyl red, and still more for the yet higher range of phenolphthalein. Obviously, then, the calculated molarities for the sodium hydroxide solution will not be the same for the three indicators. A solution prepared as 0.1000 *M* with methyl orange as the indicator will not have this molarity for either of the other two indicators.[21]

A further interesting experiment, using phenolphthalein as the indicator, is to titrate the acid with the base and then repeat the comparison in reverse order. If the sodium hydroxide solution is free of carbonate, little will be noted, but the two values may be as much as 5 per cent apart when commercial sodium hydroxide is used for the solution of the base. This difference is attributable to the presence of sodium carbonate. With methyl orange the full basicity is shown in the titration, but with phenolphthalein the solution turns colorless as soon as the hydrogen carbonate stage, HCO_3^-, is passed. Use is made of these facts in Chapter 25 for the titration of a mixed base and a carbonate.

Sensitivity of Indicators

In the older literature, statements appear to the effect that certain indicators are sensitive to acids or bases, whereas others are not. Thus, phenolphthalein is said to be sensitive to hydrogen ions and methyl orange to hydroxyl ions. What is meant here by the word "sensitivity" can be better specified by giving the *p*H range of the indicator. On this basis, an indicator sensitive to hydrogen ions has a high *p*H range.

More likely today the word is used to refer to the length of the *p*H range, through which the indicator undergoes its color transformation. Thus, neutral red changes between 6.8 and 8.0, but litmus changes between *p*H 5 and 9. The former would then be considered more sensitive to *p*H changes. Other factors being equal in effect, short-range indicators are preferable for sharp end points.

[21] Many students obtain molarities in the general region of 0.1000, 0.0998, and 0.0994, for methyl orange, methyl red, and phenolphthalein, respectively.

USE OF NONAQUEOUS SYSTEMS

Discussion of acid-base titrations has been limited thus far to reactions in aqueous solution. Even though any worthwhile treatment of other systems is beyond the scope of this book, it should be mentioned that their application is being largely extended, both in the use of nonaqueous solvents and of titrants other than the common acids and alkalies.[22]

With this technic, it may easily be possible to titrate substances having dissociation constants less than 10^{-8}, which is about the lower limit for successful work in aqueous solution. Several examples are of interest. In ethylenediamine, boric acid, H_3BO_3, gives three potentiometric inflection points, as compared to a very poor inflection point in aqueous solution (see Figure 13.2). In the same solvent a mixture of phenol and a carboxylic acid gives two inflection points. Phenols are acids too weak to be titrated in aqueous solution (see Figure 13.2); but they can be titrated in an anhydrous, strongly basic solvent, such as ethylenediamine, with a titrant such as sodium aminoethoxide $H_2NCH_2CH_2ONa$, with either colorimetric or potentiometric detection of the end point.[23]

[22] Fritz, *Acid-Base Titrations in Nonaqueous Systems*, G. F. Smith Chemical Co., 1952. Riddick, *Anal. Chem.* **24**, 41 (1952).

[23] Moss *et al.*, *Anal. Chem.* **20**, 784 (1948).

CHAPTER 14

TITRIMETRY: OXIDATION-REDUCTION METHODS

Titrimetric reactions involving oxidation-reduction[1] are usually based on the fundamental reaction represented by the equation

$$\text{Reduced form} \rightleftarrows \text{oxidized form} + n \text{ electrons}$$

This equation shows that oxidation and reduction may be defined, respectively, as the loss and gain of electrons. Whenever one substance is oxidized (loses electrons), an equivalent amount of some other substance must be reduced (gain electrons). The fundamental equation for the half-cell reaction may be abbreviated to

$$\text{Red} \rightleftarrows \text{ox} + n\,e$$

In practice the process may include hydrogen or hydroxyl ions, as well as water molecules, as shown in the following examples:

$$Fe^{+2} \rightleftarrows Fe^{+3} + e$$
$$2\ Cr^{+3} + 7\ H_2O \rightleftarrows Cr_2O_7^{-2} + 14\ H^+ + 6\,e$$
$$2\ OH^- \rightleftarrows H_2O + 2\,e$$

Scope

A reaction as fundamental as that indicated above is bound to have important analytical applications. In titrimetry these applications include (1) the use of reagents to accomplish incidental oxidations or reductions in preparing a system for measurement, and (2) the use of standard solutions of oxidants or reductants for titrimetric measurements. Although the same theory underlies both cases, the latter use is emphasized in this chapter.

Redoximetry includes two subdivisions for measurement by titration: (1) *oxidimetry,* involving reactions in which the standard solution is an

[1] See Chapter 26 for laboratory exercises on redoximetry.

oxidizing agent, and (2) *reductimetry,* involving reactions in which the standard solution is a reducing agent. As noted in the examples already given, the oxidation or reduction may involve the transfer of electrons from or to atoms, or groups of two or more atoms.

In recent years there has been a trend in the literature of analytical chemistry to designate the different subdivisions or kinds of methods in titrimetric oxidation-reduction work by the name of the reagent used. In contrast, a decade or so ago "iodimetry" was one of the few terms so used. Oxidimetry and reductimetry refer, then, to the two main divisions of redoximetry. In each of the two divisions the names of subdivisions are based upon the reagents used, "permanganimetry" and "thiosulfatimetry" being examples. This nomenclature is followed in Chapter 26 for the various reactants discussed.

Equivalent Weights

During past decades various schemes have been proposed and used for determining the equivalent weights of the reactants when the normal system for specifying concentration in redox titration is used. Expressions such as "apparent valence change," [2] "state of oxidation," [3] and "oxidation number" [4] indicate systems that serve ultimately for determining the number of electrons transferred in the reaction.

In this book preference is given to the use of half-cell or electrode reactions as a basis for calculating equivalent weights. This viewpoint is consistent with the currently accepted interpretation of oxidation-reduction. Every reaction of this type involves electrode reactions. In general, then, the equivalent weight of an oxidant or reductant is equal to the formula weight of the substance divided by the number of electrons lost or gained by the substance in the specified reaction.

This method of equivalent-weight determination necessitates writing the equations for the half-cell reactions in the oxidation-reduction process, which include the number of electrons functioning. When the expression is balanced, the number of electrons required per molecule of reactant is the number by which to divide the formula weight of the reactant to obtain the equivalent weight. In the equation, account must be taken of the coefficients of the oxidant and reductant.

Electrode Reactions and Potentials

Table 14.1 includes such data for a number of common oxidation-reduction reactions, formulated as half-cell equations. The formula for the

[2] Mahin, *Quantitative Analysis,* McGraw-Hill, 1932.
[3] Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis,* Macmillan, 1952.
[4] Willard and Furman, *Elementary Quantitative Analysis,* Van Nostrand, 1940.

TABLE 14.1

DATA ON OXIDATION-REDUCTION REACTIONS

Usual Form of Reactant	*Electrode Reaction*	*Molar Potential E^0* (in volts)
Al	$Al \rightleftharpoons Al^{+3} + 3\,e$	+1.67
Zn	$Zn \rightleftharpoons Zn^{+2} + 2\,e$	0.76
$Na_2C_2O_4$	$H_2C_2O_4 \rightleftharpoons 2\,CO_2 + 2\,H^+ + 2\,e$	0.49
$CrCl_2$	$Cr^{+2} \rightleftharpoons Cr^{+3} + e$	0.41
Sn	$Sn \rightleftharpoons Sn^{+2} + 2\,e$	0.136
H_2	$H_2 \rightleftharpoons 2\,H^+ + 2\,e$ ($[H^+] = 1$)	0.000
$TiCl_3$	$Ti^{+3} + H_2O \rightleftharpoons TiO^{+2} + 2\,H^+ + 2\,e$	−0.04
H_2S	$H_2S \rightleftharpoons S + 2\,H^+ + 2\,e$	−0.14
H_2SnCl_4	$Sn^{+2} \rightleftharpoons Sn^{+4} + 2\,e$ (0.5 *M* HCl)	−0.15
$Na_2S_2O_3$	$2\,S_2O_3^{-2} \rightleftharpoons S_4O_6^{-2} + 2\,e$	−0.17
Ag	$Ag + Cl^- \rightleftharpoons AgCl + e$	−0.222
Hg	$2\,Hg + 2\,Cl^- \rightleftharpoons Hg_2Cl_2 + 2\,e$ (sat'd)	−0.244
$K_4Fe(CN)_6$	$Fe(CN)_6^{-4} \rightleftharpoons Fe(CN)_6^{-3} + e$	−0.36
O_2	$4\,OH^- \rightleftharpoons O_2 + 2\,H_2O + 4\,e$ ($[OH^-] = 1$)	−0.40
KI_3*	$3\,I^- \rightleftharpoons I_3^- + 2\,e$	−0.535
Na_3AsO_3	$HAsO_2 + 2\,H_2O \rightleftharpoons H_3AsO_4 + 2\,H^+ + 2\,e$	−0.56
H_2O_2	$H_2O_2 \rightleftharpoons O_2 + 2\,H^+ + 2\,e$	−0.68
Quinhydrone	$C_6H_4(OH)_2 \rightleftharpoons C_6H_4O_2 + 2\,H^+ + 2\,e$	−0.70
$FeSO_4$	$Fe^{+2} \rightleftharpoons Fe^{+3} + e$	−0.77
Ag	$Ag \rightleftharpoons Ag^+ + e$	−0.80
Diphenylamine-sulfonate†	$2\,C_{12}H_{11}O_3SN \rightleftharpoons C_{24}H_{20}O_6S_2N_2 + 2\,H^+ + 2\,e$	−0.84
	$CuI \rightleftharpoons Cu^{+2} + I^- + e$	−0.88
$HgCl_2$	$Hg_2^{+2} \rightleftharpoons 2\,Hg^{+2} + 2\,e$	−0.91
$VOSO_4$	$VO^{+2} + 2\,H_2O \rightleftharpoons H_3VO_3 + H^+ + e$	−1.00
Br_2	$2\,Br^- \rightleftharpoons Br_2 + 2\,e$	−1.06
Fe-1,10-phenanthroline‡	$Fe(C_{12}H_8N_2)_3^{+2} \rightleftharpoons Fe(C_{12}H_8N_2)_3^{+3} + e$	−1.06
KIO_3	$I^- + 3\,H_2O \rightleftharpoons IO_3^- + 6\,H^+ + 6\,e$	−1.09
O_2	$2\,H_2O \rightleftharpoons O_2 + 4\,H^+ + 4\,e$ ($[H^+] = 1$)	−1.23
$K_2Cr_2O_7$	$2\,Cr^{+3} + 7\,H_2O \rightleftharpoons Cr_2O_7^{-2} + 14\,H^+ + 6\,e$	−1.36
Cl_2	$2\,Cl^- \rightleftharpoons Cl_2 + 2\,e$	−1.36
	$Hg_2Cl_2 \rightleftharpoons 2\,Hg^{+2} + 2\,Cl^- + 2\,e$	−1.436
$Ce(SO_4)_2$	$Ce^{+3} \rightleftharpoons Ce^{+4} + e$ (1 *M* H_2SO_4)	−1.45
$KBrO_3$	$Br^- + 3\,H_2O \rightleftharpoons BrO_3^- + 6\,H^+ + 6\,e$	−1.52
$KMnO_4$	$Mn^{+2} + 4\,H_2O \rightleftharpoons MnO_4^- + 8\,H^+ + 5\,e$	−1.52
	$MnF_6^{-2} + 4\,H_2O \rightleftharpoons MnO_4^- + 5\,F^- + 8\,H^+ + 4\,e$	?
	$MnO_2 + 2\,H_2O \rightleftharpoons MnO_4^- + 4\,H^+ + 3\,e$ (neutral)	−1.67
	$MnO_4^{-2} \rightleftharpoons MnO_4^- + e$	?
K_5IO_6§	$IO_3^- + 3\,H_2O \rightleftharpoons H_6IO_6 + H^+ + 2\,e$	−1.71
H_2O_2	$2\,H_2O \rightleftharpoons H_2O_2 + 2\,H^+ + 2\,e$	−1.77
$(NH_4)_2S_2O_8$	$2\,SO_4^{-2} \rightleftharpoons S_2O_8^{-2} + 2\,e$	−2.00
F_2	$2\,F^- \rightleftharpoons F_2 + 2\,e$	−2.85

* Written as $KI \cdot I_2$ in Chapter 26.
† Diphenylamine-p-sulfonic acid ⇌ diphenylbenzidine violet-p,p′-disulfonic acid.
‡ Ferrous-1,10-phenanthroline.
§ Often written as KIO_4.

reactant refers to the compound that is used in the system as an oxidant or reductant. The formula of the oxidized form functioning in the reaction is shown on the right-hand side of the equation, and that for the reduced form on the left-hand side. The equation shows the number of electrons involved. Such half-cell equations may be given in apparently different forms to emphasize different viewpoints, or for convenience, as, for example

$$2\ Cl^- \rightleftarrows Cl_2 + 2\ e$$
$$Cl^- \rightleftarrows \tfrac{1}{2}\ Cl_2 + e$$

The molar electrode potential E^0 is the same in both cases. These potentials, as given in Table 14.1, are discussed subsequently from the viewpoint of their application. In general, the more positive the E^0 value for the half-cell reaction, as shown in Table 14.1, the greater the tendency for the reaction to proceed to the right; the more negative the E^0 value, the greater the tendency to proceed to the left.

If the half-cell equations are written as reduction reactions, the general form becomes

$$Ox + n\ e \rightleftarrows red$$

The numerical value of E^0 is the same as that in Table 14.1 but the sign is changed. This is done to keep the equation thermodynamically correct. Then, a positive E^0 value still indicates a tendency for the reaction to proceed from left to right, as written, and a negative E^0 value indicates a tendency to go from right to left.

The student should keep in mind that the molar electrode potentials of Table 14.1 refer to the half-cell reaction carried out under standard conditions, i.e., at unit activity of each of the reactants and products indicated. In any usual solution, the molar electrode potential may not be strictly applicable because of the interaction of the substances with each other or the solvent, as in complexation reactions. For example, in hydrochloric acid solution ferric ion forms complex ions, such as $FeCl^{+2}$, and $FeCl_2^+$, and $FeCl_4^-$, with the chloride ion present. Furthermore, insolubility and hydrolysis may play significant roles in altering the observed potential. Swift[5] discusses the use of formal electrode potentials, the suggested advantage being the attainment of more practically applicable standard potentials.

COURSE OF OXIDATION-REDUCTION REACTIONS

The general nature of the course of the reactions being considered in this chapter may be presented most conveniently from the standpoint of oxidation-reduction potentials.

[5] Swift, *A System of Chemical Analysis*, Prentice-Hall, 1939.

The essential chemical processes concerned in oxidation and reduction may be expressed in terms of single or half-cell electrode reactions, as previously discussed. For the oxidation of the ferrous ion the equation is

$$Fe^{+2} \rightleftarrows Fe^{+3} + e$$

Electrode potentials for such systems may be determined in accordance with the Nernst equation. For the ferric-ferrous system the electrode potential is

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_{Fe^{+3}}}{a_{Fe^{+2}}}$$

or, at 25° and substituting concentrations for activities, and since n is 1 for this reaction,

$$E = E^0 - 0.059 \log \frac{[Fe^{+3}]}{[Fe^{+2}]}$$

where E is now the potential at 25° for the prevailing ratio of the oxidized form to the reduced form, E^0 is the standard potential for a system containing equal activities or equimolar concentrations of the oxidized and reduced forms, and n is the number of electrons transferred for the reaction as written. E^0 is equal to −0.77 volts for the ferric-ferrous system, referred to the normal hydrogen electrode.

The value of E^0 for the ferric-ferrous system varies markedly with the anion present because of complexation of one or both of the iron species. Thus, it is −0.70 in 1 M hydrochloric acid and −0.61 in a solution which is 1 M in sulfuric acid and 0.5 M in phosphoric acid.

Such potentials are conveniently determined experimentally (see Chapter 30) by means of a cell combination such as that represented by the expression

$$Hg/Hg_2Cl_2,\ KCl//Fe^{+3},\ Fe^{+2}/Pt$$

in which the combination on the right-hand side is the unknown cell and that on the left-hand side is the calomel cell, the potential of which is known for a given concentration of potassium chloride. In practice, some suitable measuring device, such as a potentiometer, is used to determine the potential difference existing when a calomel and a platinum electrode dip into the solution being investigated.

Electrode potentials have been determined for a considerable number of oxidation-reduction systems. Data for some of them are given in Table 14.1. Latimer[6] has published a comprehensive monograph on the topics of electrode potentials and of the oxidation states of the elements.

[6] Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, Prentice-Hall, 1952.

If one refers again to the statement of the Nernst equation, it is evident that $E = E^0$ when the activities or concentrations of the two iron species are equal, that is, when $[Fe^{+3}] = [Fe^{+2}]$. The potential depends upon the ratio of the activities or concentrations, and not upon the absolute amounts present. If $[Fe^{+3}]$ is 0.1 M and $[Fe^{+2}]$ is 0.01 M.

$$E = -0.77 - 0.059 \log 10 = -0.83 \text{ volts}$$

Thus, one may easily calculate the value for any stage in the oxidation of ferrous ion to ferric ion, as shown in Table 14.2. The infinite potentials indicated are never observed in practice because of the difficulty of obtaining a solution of either oxidation state which does not contain at least a minute amount of the other oxidation state. Equilibrium considerations point to this conclusion.

A more practical calculation would assume ratios of the ferric to ferrous forms to be 1 to 10^3 or 10^4 at the beginning of the titrations and 10^3 or 10^4 to 1 at the end point. This calculation is based upon the usual desired accuracy in analytical titration of one part in a thousand.

TABLE 14.2

DATA FOR DIFFERENT VALUES OF THE RATIO $[Fe^{+3}]/[Fe^{+2}]$

Per Cent Oxidized	$\frac{[Fe^{+3}]}{[Fe^{+2}]}$	$\text{Log } \frac{[Fe^{+3}]}{[Fe^{+2}]}$	E_{Fe}
0	0	$-\infty$	
1	1/99	−2.00	−0.65
10	1/9	−0.95	−0.71
30	1/2.33	−0.37	−0.75
50	1	0.00	−0.77
70	2.33	+0.37	−0.79
90	9	+0.95	−0.83
99	99	+2.00	−0.89
100	$+\infty$	$+\infty$	

If the electrode potentials at various points in the course of the titration are determined experimentally, the process amounts to making a potentiometric titration, as discussed in Chapter 18. Table 14.2 shows the data calculated for different ratios of ferric to ferrous ions in the titration of ferrous iron. The value when the ratio is unity represents the E^0 value for iron, as given in Table 14.1. The data in Table 14.2 are shown graphically in Figure 14.1, which gives the calculated oxidation potential as a function of the ratio of the oxidized form to the reduced form. In addition to the ferric-ferrous system, the location of several other sys-

tems is shown. The E^0 value for each system corresponds to the point of 50 per cent oxidation on the curves. The slope of the curves depends upon the number of electrons n involved in the factor $0.059/n$, and also upon the hydrogen ion concentration, if it is an influential factor, as in oxidations with permanganate or dichromate. The latter effect is discussed subsequently.

As an indication of the application of the curves, we may take the titration of iron with dichromate. At every stage in the titration, the potential of the ferrous-ferric system will be equal to that of the chromic-dichromate system, since an equilibrium condition is rapidly attained as each portion of titrant is added. If the two potentials were not equal, the two systems would not be in equilibrium and reaction would occur until the relative concentration ratios were such that the potential of each of the two systems was identical to that of the other.

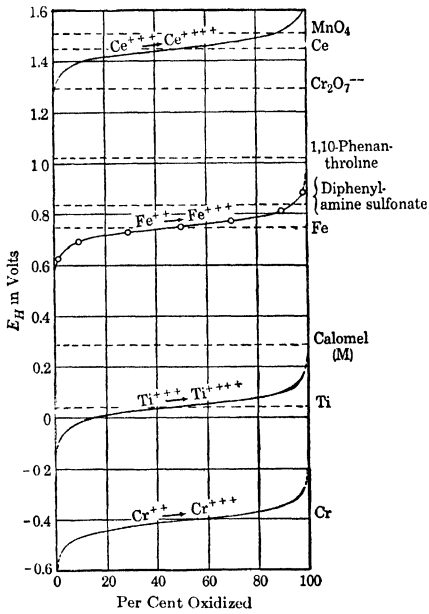


Figure 14.1

Oxidation potentials at different stages of reaction.

The curve for the titration would follow approximately the curve shown for the ferric-ferrous system until near the equivalence point, where it would rise sharply and begin the curve for the dichromate system. At an excess of only one part in a thousand of dichromate, the potential of the chromium system as well as that of the iron system, in 1 M hydrogen ion solution, would be given approximately by

$$E_{Cr} = E^0 - \frac{0.059}{6} \log \frac{[Cr_2O_7^{-2}]\,[H^+]^{14}}{[Cr^{+3}]^2}$$

$$= -1.36 - 0.010 \log (10^{-1} \text{ to } 10^{-3})$$

$$= -1.33 \text{ to } -1.35 \text{ volts}$$

The end point may be taken as the midway point in the nearly vertical portion of the curve, as in pH curves for the titration of acids with a base. In some cases this should not be done.

As indicated in the previous paragraph, half-cell reactions involving oxygen-containing species usually involve hydrogen ion and result in a more complicated form of the Nernst equation. For the permanganate system,

$$Mn^{+2} + 4\ H_2O \rightleftarrows MnO_4^- + 8\ H^+ + 5\ e$$

$$E = E^0 - \frac{0.059}{5} \log \frac{[MnO_4^-]\,[H^+]^8}{[Mn^{+2}]}$$

The concentration of water is not included, since it is effectively constant in aqueous solution and the term involving it is absorbed into another constant, the standard potential E^0. The foregoing form of the Nernst equation indicates that the oxidation potential of ions such as permanganate and dichromate is a function of the acidity of the solution. In such cases the tabular values are generally given for a solution molar with respect to hydrogen ion. Different acidities give different potentials.

Equilibrium in Redox Reactions

The equilibrium constant for oxidation-reduction reactions can be calculated from E^0 data for the two systems involved. Such computation permits (1) prediction as to whether or not a given reaction will be suitable for quantitative work, and (2) determination of the effect of varying concentrations of the different species on the course of reaction. In the general case of the titration of the reduced form of substance A with the oxidized form of substance B, the reaction is given by the equation

$$a\ \text{red}_A + b\ \text{ox}_B \rightleftarrows a\ \text{ox}_A + b\ \text{red}_B$$

where red_A and ox_A represent the reduced and oxidized forms of A, and similarly for B. The coefficients needed to balance the expression are represented by a and b. The equations for half-cell reactions involved are, accordingly,

$$\text{Red}_A \rightleftarrows \text{ox}_A + n_A e \qquad E^0 = E^0{}_A$$

and

$$\text{Red}_B \rightleftarrows \text{ox}_B + n_B e \qquad E^0 = E^0{}_B$$

From the equation for the reaction, it is evident that $a \times n_A = b \times n_B$. At any point in the titration,

$$E_A = E^0{}_A - \frac{0.059}{n_A} \log \frac{[\text{ox}_A]}{[\text{red}_A]}$$

and

$$E_B = E^0{}_B - \frac{0.059}{n_B} \log \frac{[\text{ox}_B]}{[\text{red}_B]}$$

and

$$E_A = E_B$$

The log term in each Nernst equation can be multiplied by a unity factor consisting of the numerical coefficient for the particular half-cell system in the equation for the reaction, giving

$$E_A = E^0_A - \frac{0.059}{a\,n_A} \log \frac{[\text{ox}_A]^a}{[\text{red}_A]^a}$$

and

$$E_B = E^0_B - \frac{0.059}{b\,n_B} \log \frac{[\text{ox}_B]^b}{[\text{red}_B]^b}$$

Since at equilibrium $E_A = E_B$, equating the right-hand members of the two Nernst expressions and rearranging gives

$$\frac{n\,(E^0_A - E^0_B)}{0.059} = \log \frac{[\text{ox}_A]^a\,[\text{red}_B]^b}{[\text{red}_A]^a\,[\text{ox}_B]^b}$$

where $n = a\,n_A = b\,n_B$. Then,

$$\frac{n\,(E^0_A - E^0_B)}{0.059} = \log K$$

The value of K can be calculated, using the appropriate values for E^0. Furthermore, the equilibrium ratios of the two forms of each system can be calculated, since

$$\frac{[\text{ox}_A]_{eq}}{[\text{red}_A]_{eq}} = \frac{[\text{red}_B]_{eq}}{[\text{ox}_B]_{eq}} = \sqrt[(a+b)]{K}$$

To illustrate the application of the foregoing expressions, the question can be answered as to the possible success, i.e., quantitative nature, of the titration of a titanyl solution by a standard chromous solution in 1 M acid. The equilibrium constant for the reaction is calculated, using the E^0 values of Table 14.1.

$$TiO^{+2} + Cr^{+2} + 2\,H^+ \rightleftarrows Ti^{+3} + Cr^{+3} + H_2O$$

$$\log K = \frac{1\,(E^0_{Ti} - E^0_{Cr})}{0.059}$$

$$= \frac{(0.04 + 0.40)}{0.059} = 7.5$$

$$K = 10^{7.5}$$

$$\frac{[Ti^{+3}]_{eq}}{[TiO^{+2}]_{eq}} = \sqrt[2]{10^{7.5}} = 10^{3.8}$$

At equilibrium, less than one part in a thousand of the titanyl ion will be left unreduced.

Equivalence-Point Potential

As discussed in the previous sections, at any stage in a redox titration, when the two reactants come to equilibrium, $E_A = E_B$. At the point

where a stoichiometrically or chemically equivalent amount of B has been added to the solution of A, the potential existing in each system may be designated as the equivalence potential, E_{eq}. Then, at this stage of the reaction, $E_{eq} = E_A = E_B$.

The value of the equivalence potential in a redox reaction can be calculated from the standard potentials of the reactants involved and the nature of the reaction.

Let us consider the general reaction of the previous section,

$$a\ \text{red}_A + b\ \text{ox}_B \rightleftarrows a\ \text{ox}_A + b\ \text{red}_B$$

At the equivalence point in this reaction, the concentrations of ox_A and red_B will be to each other in the ratio of a to b; the same is true for the equilibrium concentrations of red_A and ox_B. Letting x represent the fraction of A and B which have reacted, the potentials in the two systems will then be represented by

$$E_{eq} = E_A = E^0_A - \frac{0.059}{n_A} \log \frac{x}{1 - x}$$

and

$$E_{eq} = E_B = E^0_B - \frac{0.059}{n_B} \log \frac{x}{1 - x}$$

Multiplying the first equation by n_A and the second equation by n_B and adding the resultant equations,

$$E_{eq} = \frac{n_A E^0_A + n_B E^0_B}{n_A + n_B}$$

or

$$E_{eq} = \frac{b E^0_A + a E^0_B}{a + b}$$

For a simple symmetrical reaction such as

$$Fe^{+2} + Ce^{+4} \rightleftarrows Fe^{+3} + Ce^{+3}$$

the equivalence potential is one-half the sum of the molar electrode potentials. For an asymmetrical reaction such as

$$2\ Cr^{+2} + Sn^{+4} \rightleftarrows 2\ Cr^{+3} + Sn^{+2}$$

the expression is

$$E_{eq} = \frac{E^0_{Cr} + 2 E^0_{Sn}}{1 + 2}$$

$$= \frac{-0.41 + 2(0.15)}{3}$$

$$= -0.04 \text{ volts}$$

Knowledge of the equivalence potential is useful in selection of the proper indicator for a titration, as later discussion will show.

DETERMINATION OF END POINTS

In the application of oxidation-reduction methods, the analyst has a somewhat greater choice of procedures for determining end points than is the case in neutralization processes. Although all the methods mentioned are used at some time, one usually finds that some given method is followed more or less generally in a specific case. In titrating ferrous ion with permanganate, however, the analyst could use any of the methods suggested. Those most generally used are summarized here.

Use of a Colored Reactant

In oxidation-reduction determinations we find the most important examples of the method of detecting end points by means of color changes which are connected with the reactants themselves. The utility of potassium permanganate as an oxidant rests first, perhaps, upon its high oxidation potential, but hardly less upon its self-indicating properties. The intensity of the color of the permanganate ion is exceptional among simple ions. The dichromate, triiodide, and ceric ions are likewise colored, but the property is by no means as useful analytically in their cases as in the case of permanganate.

It should be noted that some individuals, in titrating a triiodide ion solution with thiosulfate, prefer to rely upon the change in hue of the system itself to indicate the end point rather than to use starch as an internal indicator compound. In the former case, a small amount of an organic liquid that is immiscible with water and has a greater relative solubility for iodine than has water (e.g., carbon tetrachloride) may be added. The iodine remaining concentrates in the small volume of organic liquid, thus intensifying the color and thereby making the end point easier to detect.

Use of Potentiometric Indicator

In view of what has been presented already regarding electrode potentials and the course of redox reactions, it is evident that end points of such reactions can be determined potentiometrically. In fact, difficulties with other means of detecting end points in certain systems probably served to bring about the industrial adoption of potentiometric methods in a number of cases.

The details of manipulation of this method are given in Chapter 30. It is of interest to note that the electrode pair used for oxidation-reduction reactions is usually simpler than for other reactions.

Use of an Indicator Compound

Even though detection of certain end points potentiometrically, or by means of color changes of the reactants themselves, as in the titration of triiodide with thiosulfate, may be possible, many individuals prefer to use an indicator compound. For the iodine titration mentioned, a suspension of starch is used internally. This indicator is especially noteworthy in that it is said to give the most sensitive end-point color change known in titrimetry. The uses of sodium diphenylaminesulfonate with dichromate ion and of the tris-1,10-phenanthroline-ferrous complex with ceric ion, are additional examples of internal indicators.

The functioning of indicators, such as diphenylaminesulfonate and ferrous-1,10-phenanthroline, may be interpreted in terms of oxidation-reduction potentials. When such indicators are used, there are generally present in solution three systems undergoing oxidation-reduction change; the substance titrated, in its reduced and oxidized forms; the indicator, in its reduced and oxidized forms; and the titrant, in its oxidized and reduced forms. For a given titration, the indicator should have an oxidation potential that lies between the oxidation potentials for the substance to be titrated and for the titrant. More specifically, its standard potential should be slightly beyond that of the equivalence potential in the direction of the standard potential of the titrant. Summaries of data on redox indicators are available.[7]

From Figure 14.1 it is evident that, in the oxidation of ferrous ion with ceric ion, the E^0 value for 1,10-phenanthroline should lie between 0.95 and 1.30 volts. Actually the E^0 value for the equilibrium

$$Fe(C_{12}H_8N_2)_3^{+2} \rightleftarrows Fe(C_{12}H_8N_2)_3^{+3} + e$$

is in the region of -1.06 volts. This value is satisfactory, since the potential at which only one part in a thousand of ferrous ion is unoxidized is

$$E_{Fe} = -0.77 - 0.059 \log 10^3 = -0.95$$

and the equivalence point potential is about -1.1 volts.

The action of certain other indicators is interpreted differently. Starch, for example, is said to form with iodine a complex in which the iodine is located within a helical type of structure. To this complex may be attributed the blue color.

In many redox titrations the production of the end point requires the addition of a certain excess of titrant. The amount of excess may be

[7] Whitehead and Willis, *Chem. Rev.* **29**, 69 (1941); Smith and Richter, *Phenanthroline and Substituted Phenanthroline Indicators*, G. F. Smith Chemical Co., 1944; Fales and Kenny, *Inorganic Quantitative Analysis*, pp. 391-394, Appleton-Century, 1939; and Tomicek, *Chemical Indicators*, Butterworths Scientific Publications, 1951.

negligible, or it may be of sufficient magnitude that a blank titration is required for its determination. Correction must then be made for the error.

If an indicator is to be used, one that functions internally, that is, in the solution titrated, is always preferable. If this is not possible, the analyst must resort to an external technic. The customary procedure is to place drops of the indicator solution in depressions of a spot plate, or on some other suitable surface. Then at intervals during the titration a drop of the solution is removed on a stirring rod and touched to a drop of the indicator. Some characteristic reaction, such as the formation of a precipitate or a change of color, indicates the attainment of the end point.

APPLICATIONS

Redoximetry has available probably a greater number of possible standard solutions than any other area of titrimetry. These standard oxidants and reductants cover practically the whole useful potential range from +0.4 volts for the chromous reducing solution to −1.6 volts for the permanganate oxidizing solution under neutral or slightly alkaline conditions. Reducing agents more powerful than chromous ion tend to evolve hydrogen from their solution.

A partial list of titrimetric oxidizing agents includes solutions of permanganate, hypochlorite, bromate, ceric, dichromate, iodate, bromine, ferric, and iodine ions and species. Standard reducing solutions include chromous, titanous, stannous, thiosulfate, ferrocyanide, arsenite, and ferrous ions.

Standard reductants are usually instable because of air oxidation and, with the exception of thiosulfate and arsenite solutions, must be kept under an atmosphere of nitrogen or carbon dioxide if the concentration of active species is not to change.

The requirements for primary standards for redox solutions and the conditions for their optimum use have been well summarized by Stenger.[8]

[8] Stenger, *Anal. Chem.* **23**, 1540 (1951).

CHAPTER 15

TITRIMETRY: PRECIPITATION AND COMPLEXATION METHODS[1]

Precipitation and complexation methods of titrimetry are based, in general, on one of two types of reactions. The reactions go to completion as the result of the practically complete removal of a product through the formation of (1) an insoluble precipitate, or (2) a soluble, slightly dissociated complex ion or compound. An example of the former type is the reaction between chloride and silver ions; of the latter type, the formation of the ion $Ni(CN)_4^{-2}$ in the titration of nickelous ion with cyanide ion.

Although many determinations employing precipitation or complexation procedures are possible, the number of methods in wide use is much smaller than is the case for neutralization or oxidation-reduction methods. A few of them, however, are relatively important. Several typical procedures are described.

Equivalent Weights

In precipitation and complexation methods are to be found the most confusing cases encountered in determining equivalent weights. Several reactions involving the cyanide ion may be taken as an illustration of this confusion.

If silver ion is titrated, with an alkali cyanide solution, the reaction proceeds according to the equation

$$Ag^+ + CN^- \rightarrow AgCN \downarrow$$

and the equivalent weight of the cyanide is obviously the formula weight. In such simple cases, the formula weight divided by the metathetical valence of the constituent functioning gives the equivalent weight.

If the process is reversed, as in the determination of cyanide, the reac-

[1] See Chapter 27 for laboratory exercises involving precipitimetry and complexiметry.

tion starts in the same way, according to the reaction

$$CN^- + Ag^+ \rightarrow AgCN \downarrow$$

Since the cyanide is in excess, a further reaction

$$AgCN + CN^- \rightarrow Ag(CN)_2^-$$

takes place at once. Consequently, the actual reaction involves the combination of each silver ion added with two of the cyanide ions in the sample solution, according to the equation

$$2\ CN^- + Ag^+ \rightarrow Ag(CN)_2^-$$

The equivalence point of the process is indicated by the first formation of a permanent precipitate, as

$$Ag(CN)_2^- + Ag^+ \rightarrow 2\ AgCN \downarrow$$

Consequently, one mole of silver nitrate is equivalent to two moles of cyanide.

The use of potassium cyanide to determine copper shows a different type of stoichiometry. The reaction is stated to proceed according to the molecular equation

$$2\ Cu(NH_3)_4(NO_3)_2 + 7\ KCN + H_2O \rightarrow K_4Cu_2(CN)_6 + NH_4OCN + 6\ NH_3 + 3\ KNO_3 + NH_4NO_3$$

If half the atomic weight of copper is taken as its equivalent weight, the equivalent weight for the cyanide must be ¾ of its formula weight.

In the familiar titration of zinc with potassium ferrocyanide $K_4Fe(CN)_6$, the reaction is written

$$3\ ZnCl_2 + 2\ K_4Fe(CN)_6 \rightarrow 6\ KCl + K_2Zn_3[Fe(CN)_6]_2 \downarrow$$

If the equation is divided by 6 to obtain an equivalent weight for zinc, the result indicates that the equivalent weight of the ferrocyanide is one-third the formula weight.

Willard and Furman[2] state that the equivalent weight for precipitation processes is based on "the metallic ion or cation involved in the reaction," and for complexation processes on "the amount of metallic ion or cation present in one mole of the complex."

As is evident, the determination and use of equivalent weights in such reactions is confusing. Consequently, the use of the normality system of expressing concentration is recommended only in obvious cases. The more certain basis for calculations involving precipitation and complexation reactions is the molar system.

[2] *Elementary Quantitative Analysis*, p. 165, Van Nostrand, 1940.

COURSE OF PRECIPITATION AND COMPLEXATION REACTIONS

The course of the reactions included in this group may be illustrated by a consideration of the data obtained by the potentiometric method, that is, by a plot of the volume of titrant added *versus* the measured potential of a system in the solution. As a specific example we may consider the titration of 50 ml of $M/10$ sodium chloride with $M/10$ silver nitrate solution. With a silver electrode the electrode potential may be measured as the reaction progresses. Since the latter value is essentially a function of the concentrations of chloride ion and of silver ion in the solution, the pCl values can be calculated in the same manner as pH values are obtained in neutralization reactions. On plotting a curve using these experimentally determined values of pCl as ordinate and the volume of titrant as abscissa, one obtains results similar to the relationship shown in Figure 15.1. Reactions involving complexes yield similar curves. The sharpness of the break in the curves is directly proportional to the insolubility of the precipitate or the stability of the complex, and to the concentrations of the solutions.

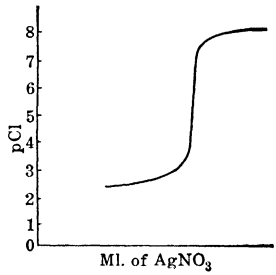


Figure 15.1

Curve for the titration of NaCl + $AgNO_3$.

Another method for obtaining the pCl values is to calculate, on the basis of the activity or the solubility product of the silver chloride formed, the concentration of the ion being precipitated for different points in the course of the precipitation. If the amount of unreacted chloride and the total volume of solution are used, reasonably close values for the chloride ion concentration are obtained. The square root of the solubility product ($K_{sp} = 10^{-10}$) gives the value at the equivalence point. After the equivalence point is passed, the value of the silver ion concentration added in excess may be substituted in the solubility product expression $[Ag^+] \cdot [Cl^-] = 10^{-10}$.

Langer and Stevenson[3] have considered theoretically the problem of locating the equivalence point in the general precipitation reaction

$$A^{+n} + B^{-n} \rightarrow AB \text{ (solid)} \downarrow$$

They concluded that the slope of the titration curve depends upon the

[3] *Ind. Eng. Chem., Anal. Ed.* **14**, 770 (1942).

ratio of the solubility product of compound AB to the initial concentration of ion A^{+n} in the solution.

DETERMINATION OF END POINTS

In this group of titrimetric methods the greatest variety of phenomena are used in some way as a means of marking the end point in reactions.

Change in a Property of the Titration System

In general, in the precipitation and complexation processes there are few examples of change of color, since most of the solutions being titrated and the titrants are colorless systems. However, in the determination of copper by means of an alkali cyanide solution, according to the equation on page 235, the end of the titration is taken at the disappearance of color of the complex $Cu(NH_3)_4^{+2}$.

Marking of the end point by a change in turbidity may be illustrated by several examples, each of which possesses individual characteristics. The simplest procedure is to add precipitant (titrant) to the solution just to the point where no more precipitate forms. In practice this process is usually too tedious to use unless the precipitate coagulates and settles quickly. A variation in this technic involves the appearance of a precipitate. Thus, when iodide ion is titrated with mercuric ion, a soluble complex is first formed, according to the equation

$$4\ I^- + Hg^{+2} \rightleftarrows HgI_4^{-2}$$

At the end point a red precipitate appears on addition of the first excess of mercuric ion, the reaction being represented by the equation

$$Hg^{+2} + HgI_4^{-2} \longrightarrow 2\ HgI_2 \downarrow$$

Another variation is the Gay-Lussac procedure for silver, which is based upon the principle of equal turbidities. In essence, the process consists of titrating to the point where equal turbidities are produced by the addition of small equal volumes of equivalent concentration solutions of the titrant and of the substance being titrated, to equal volumes of the supernatant liquid in the sample solution.

From what was stated concerning possibilities of following the course of reactions, we would expect to be able to determine equivalence points potentiometrically, using the procedure described in Chapter 30. The chief difficulty is to find a suitable indicator electrode for any given system. An indicator electrode is one that attains electrochemical equilibrium with, or as part of, a half-cell reaction system containing a species whose concentration is to be measured. Consequently, the potential

measured via the electrode is a function of the concentration the magnitude of which is desired. Further details may be found in Chapter 30. Likewise, it is possible to make conductometric titrations, as outlined in the same chapter.

Change in Appearance of an Indicator Compound

Indicator compounds are used both internally and externally in this group of methods, several different kinds of phenomena being involved, as illustrated by the examples to follow.

The use of external indicators has become relatively rare. This rare usage may be attributed partly to difficulties involved in their use, but probably much more to the development of superior means of indicating the end point.

An application of change in turbidity to mark the equivalence point is found in the titration of the ion $Ni(NH_3)_4^{+2}$ with an alkali cyanide, according to the equation

$$Ni(NH_3)_4^{+2} + 4\ CN^- \rightarrow Ni(CN)_4^{-2} + 4\ NH_3$$

A small amount of silver iodide, added to the solution being titrated, disappears sharply with excess titrant, which converts the silver into a soluble, stable complex

$$AgI + 2\ CN^- \rightarrow Ag(CN)_2^- + I^-$$

Since the equivalence point and the end point do not coincide, a suitable correction must be applied, or the titrant solution must be standardized on a nickel sample under comparable conditions.

Methods based on color changes are more numerous. The colored species formed by interaction of excess titrant with the indicator compound may be either a soluble substance or a precipitate. When silver ion is titrated with thiocyanate ion to form silver thiocyanate, a ferric ion solution is added as the indicator. At the equivalence point the excess thiocyanate reacts according to the equation[4]

$$SCN^- + Fe^{+3} \rightarrow Fe(SCN)^{+2}$$

to form the characteristic reddish-colored, soluble complex. For the method to be useful, it is evident that the precipitation of silver thiocyanate must be practically complete before the soluble complex forms. Whether or not this is true, and how to alter conditions to make it true, can be seen from calculations based on the equilibrium constants for the solubility and complexation processes involved.

[4] See Frank and Oswalt, *J. Am. Chem. Soc.* **69**, 1321 (1947). Certain other writers believe that the complex formed depends upon the excess of thiocyanate added.

Three interesting variations are found in the commonly used methods for detecting the end point in the titration of a chloride ion solution with silver nitrate solution. In the Volhard method an excess of silver solution is added. The excess silver ion is then determined with a standard thiocyanate solution, using ferric ion as indicator, as already described.

In the Mohr method the end point is marked by the formation of a colored precipitate. Potassium chromate solution is added as the indicator. The titration proceeds with the formation of silver chloride until the reaction is practically complete. Then insoluble silver chromate begins to form, imparting a reddish tinge to the solution.

This method is based upon the relative solubilities of the two compounds concerned. Silver chloride is more insoluble than the chromate and consequently forms first. The concentration of chloride in the solution thus decreases as titration proceeds, while the concentration of silver ion needed to exceed the solubility product of silver chloride slowly increases. Finally, the concentration of silver ion is sufficiently high to exceed the solubility product of silver chromate, and silver chromate begins to precipitate. From this point on, equilibrium has been attained between the concentration of silver ion and both precipitates, and silver chloride and silver chromate precipitate out of solution together. The ratio of the chloride and chromate concentrations at the point where the more soluble compound begins to precipitate may be calculated from the solubility products. At this point of equilibrium

$$\frac{K_{sp}(AgCl)}{[Cl^-]} = [Ag^+] = \sqrt{\frac{K_{sp}(Ag_2CrO_4)}{[CrO_4^{-2}]}}$$

Inserting the values for the solubility products

$$\frac{[Cl^-]}{[CrO_4^{-2}]^{1/2}} = \frac{10^{-10}}{(2 \times 10^{-12})^{1/2}} = 7 \times 10^{-5}\ M$$

The amount of chloride still unprecipitated at the end point may be calculated on the basis of the concentration of chromate ion.

The third, or Fajans, method is an example of the use of adsorption indicators. Some organic compounds of the dye-type are adsorbed by certain precipitates of colloidal nature more strongly on one side of the equivalence point than on the other. The adsorptive process apparently produces a strain or distortion in the structure of the adsorbed compound that results in a change in color on the surface of the precipitate. In the case of silver chloride precipitated by adding silver ion to chloride solution, the chloride ion is adsorbed so long as it is in excess and the particles are negatively charged. As soon as the silver ion is in excess, it is adsorbed by the colloidal particles of silver chloride.

The resulting positively charged particles then adsorb the negatively charged ions of the anionic dye (e.g., dichlorofluorescein) added. The change in structure which now occurs apparently gives rise to the transformation in color.

Obviously, the success of the method depends upon keeping the precipitate in the colloidal state.[5]

APPLICATIONS

One of the most widely used standard solutions in precipitation and complexation titrations is silver nitrate. This solution is used for the determination of chloride, bromide, iodide, thiocyanate, and cyanide ions. Certain other solutions have a very limited application, being used in some cases for only a single determination; examples are barium chloride for sulfate and thorium nitrate for fluoride. Mercurous nitrate is used to precipitate chloride and bromide, and mercuric nitrate is used to determine the same two anions by complexation. Cyanide and ferrocyanide solutions have some applications.

Solutions of soap or the equivalent salt, e.g., potassium palmitate, have been used to determine the "hardness" of water, based upon their precipitation of the calcium and magnesium. Ethylenediamine tetraacetic acid has come into widespread use for the titration of calcium and magnesium in dilute solution; the sodium salt of the compound, called "Versene," forms slightly dissociated compounds with the two cations. Designating the acid $(CH_2N)_2(CH_2COOH)_4$, as H_4Y, the equation for the reaction with magnesium is

$$Mg^{+2} + Na_2H_2Y \rightarrow MgNa_2Y + 2\ H^+$$

The indicator is a blue dye that forms a soluble red complex with magnesium ion. The equivalence point is taken as the change of the solution color from red to blue. This point marks the complete complexing of the calcium and magnesium ions.

[5] For a review of the applications of adsorption indicators, see the chapter by Fajans in *Newer Methods of Volumetric Chemical Analysis,* Van Nostrand, 1938; a revised German edition, *Neuere massanalytische Methoden,* Enke, 1951, is available.

CHAPTER 16

GRAVIMETRY

The terms "gravimetry" and "gravimetric" are used in accordance with the definitions in Webster's unabridged dictionary. Here one finds that *gravimetry* is "the measurement of weight." [1] *Gravimetric* analysis is "analysis in which the amounts of the constituents are determined by weighing." [2]

These definitions are emphasized in order to explain the treatment of gravimetry[3] in this book. Through many decades loosely defined connotations have become attached to the words. Consequently, one is likely to find, particularly in textbooks, divergent usages. In general, the difficulty stems from the failure of writers to distinguish between separation and measurement. Separation, of course, is a preparative process preceding measurement.

If the Webster definitions are accepted, there is obviously no implication about *any* kind of preparative treatment used to get the constituent into weighable form. In contrast, a number of writers have stated that gravimetric methods include the procedures in which one weighs a *compound* obtained by precipitation, with the further limitation that the ion-product equilibrium principle apply to the compound.

The significance of such limitation should be apparent. In the first place, a substance separated by precipitation need not be a compound. Selenium, gold, and platinum, for example, may precipitate as the elements. More important, volatilization, electrodeposition, and other means of separation are extensively used to isolate a wide variety of substances for weighing. Thousands of determinations of carbon in steel

[1] Since one measures mass rather than weight on an equal-arm balance, the logical term seems to be "massimetry."

[2] Recommended by the Nomenclature Committee of the Division of Analytical Chemistry of the American Chemical Society, *Anal. Chem.* **24**, 1348 (1952).

[3] See Chapter 28 for laboratory exercises involving gravimetry.

are made daily by volatilizing out carbon dioxide, absorbing the gas in Ascarite, and weighing the product. Probably the most popular method for determining copper, in many kinds of materials, is to separate it by electrodeposition and then weigh the metal. The official method for determination of butter fat in milk employs separation of the fat by extraction into diethyl ether. Following evaporation of the ether, the fat is weighed.

The general arrangement of this book is designed to isolate for consideration the processes of separation from the subsequent operations of measurement. This treatment is functional in the sense that the order followed typifies that followed in practical analysis. The analyst must have a substance in measurable condition prior to measurement.

We come now to the statement that *gravimetric measurement of a desired constituent consists only of weighing either this constituent, or something chemically equivalent to this constituent.* Measurement of the constituent directly is exemplified by weighing selenium precipitated by reduction of a selenium compound, copper electrodeposited on a platinum electrode, and fat extracted with diethyl ether. Measurement of a constituent through weighing a chemically equivalent substance is exemplified by silver precipitated as silver chloride, lead electrodeposited as lead dioxide, and carbon volatilized as carbon dioxide.

The most significant thing about this viewpoint may now be stated. Since gravimetry is measurement by weight, nothing more needs to be said here about the principles of such measurement. These principles have already been covered in Chapter 3, which deals with the measurement of the sample by determination of mass. The operation of weighing is the same whether the object weighed is a copper ore or the metallic copper subsequently electrodeposited, following dissolution of the sample.

The form in which a product is weighed is important, of course. But again it may be emphasized that obtaining a substance in suitable weighing form is a preparative-separative problem. It does not concern measurement, in this case weighing, as such.

APPLICATIONS

All-inclusive statements are hazardous, especially in science. However, if there is a universally applicable method of quantitative analytical measurement, gravimetry would seem to be it. By definition, all material substances, whether gases, liquids, or solids, possess mass. Consequently, at least in theory, they should be gravimetrically measurable.

The possibilities of this technic have long been recognized. The general principles of the equal-arm balance goes back for perhaps 30

centuries into Egyptian history. Quantitative determinations by this means for analytical purposes were developed much later; but it was early recognized that weighing a sample, and then weighing a constituent derived from the sample, provided a basis for calculating the percentage of the constituent.

Because of the generality of this method, and to a lesser extent, because of its place in history, gravimetry has had very extensive application. Most of quantitative analysis prior to 1850 was based on weighing. Relatively, it has lost ground heavily in recent decades to newer methods. However, examination of any general analytical treatises on applied analysis shows the importance of gravimetry.

A very important merit of gravimetry, as already mentioned, is its possibility of extensive application. Perhaps next in importance is the refinement of measurement possible without excessive manipulative precautions. Thus, a mass of 1.00000 g can be determined with a high-quality ordinary balance with little uncertainty in the last decimal place.

Gravimetric measurement is, contrary to many expressed opinions, a fairly rapid operation. Competent determinators can weigh a powdered sample in 15 to 30 seconds, and little more time is needed to weigh a product such as a precipitate of silver chloride or a deposit of copper. When writers state that gravimetric methods are often long and tedious, they are again confusing preparative and separative treatments which are not part of the measurement.

Perhaps the most serious limitation of gravimetry is its nondiscriminatory nature, as suggested in Chapter 11. Obviously, a balance will not give the mass of a desired constituent in a badly contaminated precipitate.

CHAPTER 17

COLORIMETRY

In general, the kinds of titrimetric and gravimetric processes discussed in preceding chapters are usually referred to as macromethods. With reasonably good quality macrobalances and burets, one may measure to approximately ± 0.0001 g or ± 0.01 ml, respectively. Then for a mass of 0.1000 g or a volume of 10.00 ml, the respective uncertainties represent one part in a thousand, or 0.1 per cent, of the amount measured. Such means of measurement are obviously unsuitable if the sample available is small and the desired constituent to be measured is present in the region of one part per million (0.0001 per cent)

Since such small amounts of constituents are extremely important in many substances, the analyst must deal with the attendant analytical problem. One approach is to refine the operations and instruments used for macroanalysis to a microsale. Thus, microbalances and burets have resulted. Although micro-, and even ultramicromethods have their place,[1] often a more practical approach in many cases of current industrial work is the use of methods especially suited to the determination of these trace amounts of constituents in ordinary-sized samples. Included in such trace-adapted methods are *colorimetric*[2] (photometric, absorptimetric, and spectrophotometric), *emissimetric* (spectrographic), *currentometric* (polarographic), and *radioactimetric* procedures.

The determination of these minute amounts of constituents often presents real difficulties. Some constituents, such as iron in water, can be concentrated by evaporation of the solvent to make a low-range sample more readily measurable by the usual titrimetric or gravimetric methods described in previous chapters. Concentration is inapplicable, however,

[1] See Pregl, *Quantitative Organic Microanalysis,* trans. by Grant, Blakiston, 1946; Niederl and Niederl, *Micromethods of Quantitative Organic Analysis,* Wiley, 1942; and Kirk, *Quantitative Ultramicroanalysis,* Wiley, 1950.

[2] See Chapter 29 for laboratory exercises involving colorimetry

to volatile constituents, such as oxygen or chlorine dissolved in water. These gases would be more or less completely eliminated on heating of the water sample. Also, many samples, especially those encountered in biological and organic chemistry, may decompose or otherwise change composition on heating.

Colorimetric measurements seem especially appropriate to illustrate some of the problems of determining trace amounts of constituents. At least with the simplest forms of equipment, standard-series comparimeters, for example, the procedures are probably unexcelled in economy to install and to operate. Furthermore, they have found wide and extensive industrial application for the determination of ions, radicals, and compounds, both inorganic and organic.

The present discussion is limited to a brief consideration of the principles of some of the most common kinds of colorimetric methods.

MEASURABLE SYSTEMS

In consideration of the possibilities of measuring constituents by colorimetric means, attention is limited here to solutions. Most applications of such methods involve material in this state.

The color of such systems is either inherent in the desired constituent (or something chemically equivalent to this constituent), or it must be developed by the use of appropriate chemical reagents. Some of the most important items concerned are treated briefly in the following paragraphs.

Desirable Properties

Whether a constituent itself is in suitable colored form, or whether such a system must be prepared by some chemical action, the solution destined for colorimetric measurement should meet, as far as possible, certain general requirements. These requirements concern ease and convenience of operation, and the reliability of results obtainable. The following characteristics of solutions for colorimetry are most important. They should (1) be self-colored; (2) be intensely colored; (3) be stable; (4) be unaffected by *p*H changes; (5) be measurable between 500 and 600 mμ, if visual means are used; (6) have a low temperature coefficient; (7) color-match permanent standards, if such are used; and (8) conform to Beer's law.

Kinds of Systems Available

Relatively few inorganic constituents are satisfactory as such, because they are either colorless or the color intensity is insufficient for the re-

quired sensitivity. The common, colored ions are those of elements found near the center of the Bohr form of the Periodic Table (see inside front cover). They include the transition elements and a few others nearby.

In contrast, there are many hundreds of organic compounds adequately colored for analytical purposes. Very often, however, they are not readily determinable because of interference of other components of the solution to be measured. Determination of lycopene in ripe tomatoes is a good example. This compound is sufficiently colored, but several others also present make its determination difficult.

If the system itself is not sufficiently colored, the only recourse is to do whatever is possible in the way of chemical transformations to achieve a colorimetrically measurable system. As in all other similar situations, the analyst is limited to the chemical possibilities of the constituents concerned in the sample. Here only brief mention can be made of methods for developing such colors. The accompanying outline indicates some important possibilities. The general basis is to list kinds of reactions by the reagents used to develop the color.

Use of Inorganic Reagents

Three kinds of reactions involving inorganic reagents are illustrated in the following equations:

Oxidation

$$Mn^{+2} + IO_4^- \longrightarrow MnO_4^-$$

$$\text{Ascorbic acid} + H_4[Si(W_3O_{10})_4] \longrightarrow \text{W-blue}$$

Reduction

Direct

$$H_3[P(Mo_3O_{10})_4] + SnCl_4^{-2} \longrightarrow \text{Mo-blue}$$

Indirect

$$Ca^{+2} \longrightarrow CaC_2O_4 \longrightarrow Ca_3(PO_4)_2 \longrightarrow H_3[P(Mo_3O_{10})_4] \longrightarrow \text{Mo-blue}$$

Complexation

Cationic

$$Cu^{+2} + 4\ NH_3 \longrightarrow Cu(NH_3)_4^{+2}$$

Anionic

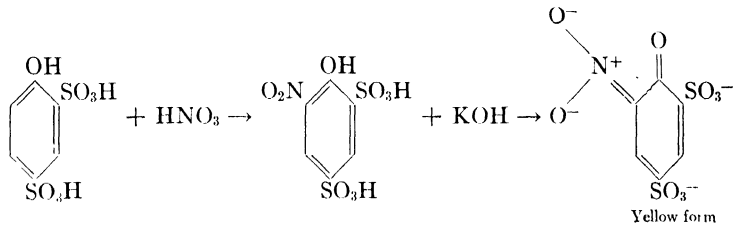
$$Co^{+2} + 4\ SCN^- \longrightarrow Co(SCN)_4^{-2}$$

Use of Organic Reagents

Three kinds of reactions involving organic reagents are illustrated in the following equations:

Salt formation

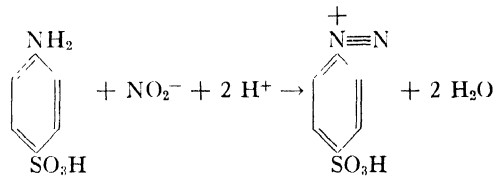
HNO_3 + phenol-2,4-disulfonic acid + KOH → color



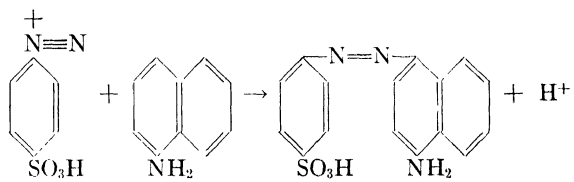
Coupling

HNO_2 + 4-aminobenzenesulfonic acid + 1-aminonaphthalene → color

Diazotization step



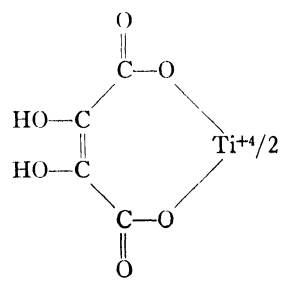
Coupling step



Chelation

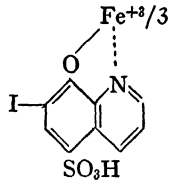
Two electrovalent bonds

Ti^{+4} + dihydroxy maleic acid → color



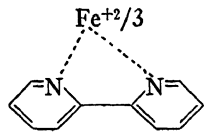
One electrovalent and one co-ordinate bond

Fe^{+3} + 7-iodo-8-hydroxyquinoline-5-sulfonic acid → color,



Two co-ordinate bonds

Fe^{+2} + 2,2′-bipyridine → color,



If color-forming reactions are used, considerable chemistry may be involved, especially in cases such as the use of molybdenum-blue for determining calcium. The diazotizing-coupling method mentioned for nitrite ion is another excellent example. The analyst has a fairly wide choice of reactants for a given constituent, e.g., iron. Likewise, many reductants, such as those listed for molybdenum and tungsten, will serve to give a heteropoly blue.

Whatever the reactants may be, the color-forming reaction(s) should meet, insofar as possible, at least the following requirements. They should (1) develop the color rapidly; (2) use a colorless reagent; (3) employ a stoichiometric reaction; (4) employ a reaction of known mechanism; (5) be independent of a particular sequence of using two or more reagents; (6) avoid special treatment, such as extraction in an immiscible solvent; (7) produce a color with maximum absorption in a particular wave-length region, if this is desirable; and (8) be free of interference.

Although many reactants in current use do not approach this ideal list of requirements, research is slowly yielding both better reagents and more information on the nature and control of variable factors. A few highly selective reagents, such as 2,2′-biquinoline for copper, have been discovered, but the long search for a specific reagent remains yet unrewarded.

Interferences

Although freedom from interference by undesired constituents has been mentioned as one of the requirements of an ideal color reaction, the

analyst must often deal with difficulties arising from the presence of interfering constituents. Only brief mention can be made of some of the ways in which the difficulties manifest themselves, and of what can be done about them.

Nature. The general nature of interference varies from case to case. The following types are of fairly common occurrence:

1. The interfering constituent is colored.
2. The color-forming reaction yields a precipitate with the interferer.
3. The color-forming reaction yields a color with the interferer.
4. The desired constituent is complexed by the interferer in such a way as to render it unreactive toward the color-forming reagent.
5. The desired constituent is oxidized or reduced by the interferer and thus rendered unreactive toward the color-forming reagent.

Prevention or control. To deal with interferences such as those suggested, the analyst has two general methods, chemical and instrumental. In some cases, the interference may be prevented, whereas in others the measuring procedure must take interference into account in some way. Operations such as the following often provide for obtaining quite satisfactory results:

1. Separation of the offender. The general methods which are applicable are the types discussed under the subject of separations.
2. Compensation of the interference. Usually this is accomplished by adding an equivalent amount of color to the standard, or by establishing instrumental calibration curves with the unwanted color present.
3. Avoidance of the interfering color. If it is sufficiently different in quality from the desired color, measurement in a particular region of the spectrum by means of a suitable selection of a filter for a photometer or setting of a spectrophotometer may suffice.
4. Adjustment of the *p*H to avoid or change the unwanted color.
5. Change of the valence of the offender to a state not giving an interfering color.
6. Complexation of the offender in a form not giving interference.
7. Determination of the amount of the interferer and correction for its effect.

TERMINOLOGY AND SYMBOLS

Because of much confusion in the usage of terms and symbols in colorimetry, special attention is given here to definitions. The suggested usage is based largely upon reports by the National Bureau of Standards[3]

[3] *Letter Circ.*, LC 857, May, 1947.

and by the Colorimetry Committee of the Optical Society of America.[4]

The ending *-tion* (occasionally *-sion*) is reserved for designation of processes. Examples are radiation, absorption, reflection, and transmission. Also included is the adjectival use, as in "absorption band." Terms ending in *-ance* refer to passive properties of objects.

Radiant energy is energy traveling through space in the form of electromagnetic waves of various wavelengths. It is the entity emitted by radiators, and it may be reflected, refracted, absorbed, or transmitted by various objects and materials. Consistent with this definition, it is appropriate to refer to ultraviolet or infrared energy, but incorrect to refer to ultraviolet or infrared radiations.

Light is the aspect of radiant energy of which a human observer is aware through the visual sensations arising from stimulation of the retina of the eye. Quantitatively, light is radiant energy evaluated in terms of the standard luminosity function (see curve *B*, Figure 17.5). The terms "ultraviolet light" and "infrared light" are not to be used, since the electromagnetic waves in these regions of the spectrum do not produce visual sensations in the eye.

The symbol for the wavelength of radiant energy is λ. The units in which wave-lengths are expressed in the visual range are millimicrons ($m\mu = 10^{-7}$ cm) or angstroms ($A = 10^{-8}$ cm).[5]

Color consists of the characteristics of light other than spatial and temporal inhomogeneities. Strictly speaking, color is a psychophysical phenomenon, an experience of the observer rather than a property of the object observed. What we really deal with, and measure, is the light-absorptive capacity of the object. White light incident upon the object is selectively absorbed, and the unabsorbed portion reaching the *macula lutea* on the retina of the human eye produces the sensation of color.[6] The quality of the unabsorbed light is determined by the nature of the absorber, and the intensity of the light by the amount of absorption.

The term "color" is an inclusive word, when accurately used. Color has three attributes, hue, lightness, and saturation. *Hue* is that attribute of certain colors which permits them to be classed as reddish, yellowish, greenish, bluish, or purplish; chromatic colors exhibit hue, but achromatic colors do not. Chemists are likely to mean "hue" when they use the word "color." *Lightness* is that attribute of any color which permits

[4] Jones *et al., J. Opt. Soc. Amer.* 34, 183 (1944); *The Science of Color,* Crowell, 1952.

[5] Frequency = speed of light/wavelength. Wave number is 1/wavelength. The unit of wavelength in this usage is usually the centimeter, and the speed of light is 3×10^{10} cm/sec.

[6] See Judd, *Color in Business, Science, and Industry,* Wiley, 1952.

it to be classified as equivalent to some member of the series of achromatic colors (grays, ranging from white to black). *Saturation* is that attribute of a chromatic color which determines its degree of difference from the achromatic color of the same lightness.

Colorimetry, as used here, is the determination of this light-absorptive capacity. *Absorptimetry* is a broader term, in that it includes the determination of the absorptive capacity for radiant energy in the ultraviolet, visible, and infrared regions of the spectrum. Often two other words, *photometry* and *spectrophotometry,* are used by chemists somewhat as synonyms for colorimetry. To be susceptible to colorimetric measurement, the constituent to be measured must itself possess a suitable color, or react with some reagent to give such a system.

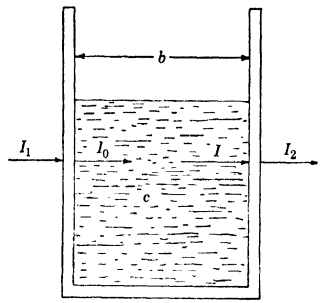


Figure 17.1

Diagram illustrating the passage of a beam of light through a solution. I_1, radiant energy incident on first surface of medium; I_0, radiant energy entering sample solution of concentration c and thickness b; I, radiant energy leaving solution and incident on second surface; I_2, radiant energy leaving last surface of medium.

To the physicist, who is concerned with the measurement of color as color, colorimetry implies the determination of the trichromatic coefficients, x, y, and z, and/or the dominant wavelength, the colorimetric purity, and the luminance of the color.[7]

Transmission terms are those relating to the rectilinear passage of homogeneous radiant energy (i.e., single frequency) through a homogeneous, isotropic, nonmetallic medium having plane, smooth, parallel sides, or through a cell having windows of such material and containing a homogeneous solution. These terms may be considered in connection with the schematic diagram of Figure 17.1.

Referring now to Figure 17.1, I_1 represents the radiant energy incident upon the first surface of the medium (e.g., the glass face of an absorption cell), I_0 that entering the sample solution, I that leaving the solution and incident upon the second surface, and I_2 that leaving the last surface of the medium.

[7] For a brief discussion of the calculation of these numerical values of a color, see Chapter 9 by D. B. Judd in Mellon, ed., *Analytical Absorption Spectroscopy,* Wiley, 1950. A more extensive treatment may be found in Judd, *op. cit.*

Then

$T_o = I_2/I_1$ = over-all transmittance (100 T_o = percentage transmittance)
$T_i = I/I_o$ = internal transmittance
$A = \log_{10} 1/T_i = -\log_{10} T_i = \log_{10} I_o/I$ = absorbance
$1 - T_i$ = absorptance (no symbol assigned)

For a solution of concentration c contained in an absorption cell of internal thickness b,

$T_{o(\text{soln})}$ = over-all transmittance of solution and cell
$T_{o(\text{solv.})}$ = over-all transmittance of solvent in same (or optically matched) cell
$T_s = T_{o(\text{soln})}/T_{o(\text{solv.})}$ = transmittancy of solute[8]
t_s = transmittancy of unit thickness
$A_s = \log_{10} 1/T_s$ = absorbancy of solute
$a_s = A_s/bc$ = absorbancy index[9] (for given thickness and concentration)
$a_M = A_s/bc$ = molar absorbancy index, if $b = 1$ cm, and $c = 1$ mole/liter
$1 - T_s$ = absorptancy (no symbol assigned)

The absorbancy can be determined, of course, for any specific set of conditions. Thus, one might have

$$A_s\ (1\%,\ 1\text{ cm},\ 425\ \text{m}\mu,\ \text{CHCl}_3,\ 1\ \text{m}\mu,\ 25^\circ) = 1500$$

in which 1% = concentration by weight, 1 cm = cell thickness, 425 mμ = wavelength at which measurement was made, $CHCl_3$ = solvent, 1 mμ = width of spectral band used, and 25° = temperature of measurement.

LAWS OF ABSORPTION

Experimental study of the absorption of light by homogeneous, transparent solids and solutions led to the formulation of two laws of fundamental importance to colorimetry. The basis of each is summarized below.

Bouguer's Law

The generalization, known as Bouguer's law, often attributed to Lambert, expresses the relationship between the absorptive capacity and the thickness of the absorbing medium. Each layer of equal thickness absorbs an equal fraction of the light which traverses it. The absorption varies directly as the logarithm of the thickness. There are no known exceptions to this law for homogeneous systems.

[8] A joint committee of the American Society for Testing Materials and the Society for Applied Spectroscopy has recommended simplifying these symbols. Thus, T signifies simply "transmittance," with no effort to make the distinction between transmittance and transmittancy noted herein. The symbol a is used without subscript (as is A) and is defined as absorptivity, rather than absorbance index.

[9] For some of the confusing symbolism used in this field, see Mellon, *op. cit.*, p. 83.

As shown in Figure 17.1, I_o and I are, respectively, the radiant energy[10] incident upon, and emergent from, a solution of concentration c and thickness b.[11] If a layer of unit thickness transmits a fraction t_s of the light incident upon it, a thickness b will transmit the fraction t_s^b. Then $I = I_o t_s^b$. This law may be expressed in the form

$$T_s = 10^{-a_s b}$$

in which T_s is the transmittancy (I/I_o), 10 is the base of common logarithms, and a_s which varies with the wavelength of the incident light, is the absorbancy index $(-\log_{10} t_s)$.[12] This law enables one to calculate from a known transmittancy and thickness to an unknown transmittancy at a different thickness.

Beer's Law

Beer's law expresses the relationship between absorptive capacity and the concentration of the solute in a solution. The absorptive capacity is directly proportional to the number of absorbing entities, such as ions or molecules. Then, if c is the concentration, transmittancy for a given thickness is t_s^c, where t_s is the transmittancy for a solution of the same thickness having unit concentration. As in the case of Bouguer's law, the absorbancy index, $-\log_{10} t_s$, applies.

This law applies if the light is approximately monochromatic, and if the nature of the absorbing entities is the same in solutions of different concentrations. It must be kept in mind that the absorbancy index, a_s, depends upon the wavelength of the incident light. Also any action in the solution, such as ionization, association, or dissociation, which affects the nature of the absorbing entities will affect the absorption. A familiar example is the change in color resulting from dilution of a solution of the dichromate ion with water. The equilibrium involved in this color transformation may be represented by the equation

$$Cr_2O_7^{-2} + H_2O \rightleftarrows 2\ HCrO_4^- \rightleftarrows 2\ H^+ + 2\ CrO_4^{-2}$$

Combined Laws

Bouguer's and Beer's laws may be combined in the expression

$$T_s = t_s^{bc} = 10^{-a_s bc}$$

[10] For many years writers have used I to signify intensity of light. Now there is a move to use P instead, and to define it as radiant flux.

[11] Absorption by the cell and reflection at the surfaces are disregarded, since in practice their effects are compensated by standardizing under working conditions.

[12] The absorbancy index, a_s, was long known as the extinction coefficient and designated by k; the symbol ϵ was then used for molar extinction coefficient.

Since $T_s = I/I_o$

$$I = I_o \times 10^{-a_s bc}$$

$$\log_{10} I_o/I = \log_{10} 1/T_s = a_s bc = A_s \text{ (absorbancy}^{13}\text{)}$$

$$c = \frac{\log_{10} 1/T_s}{a_s b}$$

Examination of these relationships shows that the measured transmittancy is a function of the absorbancy index, the cell thickness, and the concentration. Obviously, the numerical value of the absorbancy index, a_s, depends upon the units used in expressing b and c.

If one applies the last expression in order to make an analytical determination of c, the thickness b is known and A_s may be measured (often I/I_o is obtained experimentally). Then a_s (a_m for a molar solution) may be calculated for a solution of known concentration. If a_s, b, and A_s are known for an unknown solution, its concentration c may be calculated, on the assumption that Beer's law applies.

Solutions conforming to Beer's law show a constant molar absorbancy index, a_m, at all dilutions for any given thickness and wavelength. If $\log_{10} T_s$ or $\log_{10} 1/T_s$ is plotted on an equal division axis (or T_s on a logarithmic axis) against concentration, a straight line is obtained for solutions conforming to Beer's law (see Figure 17.16).

MEANS OF MEASUREMENT

Colorimetric measurements may be made in various ways. In fact, the number and variety of means available are certainly not exceeded, and probably not equaled, by those of any other type of method. They range from extremely simple means to use of instruments that are fairly complicated mechanically, optically, and electrically. In general, one may distinguish between means that measure color as color (color stimulimeters), and those that measure color as a property related to concentration of a desired constituent (absorptimeters). Only the latter type is considered here, and the discussion is limited to a few simple examples.

The basic elements of any combination designed for colorimetric measurement are as follows: (1) the *illuminant,* which is commonly a near-white, as exemplified best by sunlight and less well by the light from an incandescent tungsten filament; (2) the *colored solution* of the constituent to be measured; and (3) the *detector* for the unabsorbed light, which now is usually the eye or a photocell. The significance of kinds of illuminants and detectors is considered later.

[13] Instead of absorbancy A_s, optical density D or extinction E have been widely used.

Comparimeters

In devices and instruments which may be grouped together as comparimeters, measurement is based upon comparison of the unknown solution with one or more standards of known concentration or color value. When a color-matching pair or position is found, the same light-absorbing power in the two systems implies equal amounts of the desired constituent. From this viewpoint, a comparimeter may be considered a relative absorptimeter.

There are four kinds of technics for making such comparisons: standard series, balancing, dilution, and duplication. The first two are most useful.

Standards. The nature and the characteristics of the standards for comparison are important. Where routine determinations are to be made, standards should be in permanent form. For this purpose it is generally preferable to use the constituent that is being measured, and to have the unknown and standard(s) in the same physical state. Thus, if possible, an unknown in liquid form is compared with another liquid rather than with glasses, cards, or other dissimilar materials. To determine iron, for example, a standard solution of an iron salt, portions of which can be diluted for the required range of standards, may conveniently be kept. Often such a series retains its reliability for some days, or even months. In other cases, in order to allow for compensation of errors arising from variability in color development and stability, the analyst must prepare the standard at the same time and under the same conditions as the unknown.

Use of the desired constituent itself for standards may be impossible or inconvenient. Thus, in the determination of residual chlorine in water by means of *o*-tolidine, standard solutions of chlorine water are both very difficult to prepare and instable. For a considerable number of such cases visually equivalent standards (for at least one kind of illuminant), many of them permanent, have been prepared from various materials. The standards of the American Public Health Association for the determination of iron by the thiocyanate method consist of mixtures of solutions of potassium chloroplatinate and cobaltous chloride. Several equipment manufacturers use glass standards for numerous series. Occasionally a color card is satisfactory for rough work, as is the case with *p*H test papers. In all such instances, even when the standard and unknown are both liquids, their spectral characteristics are seldom the same. This may render matching impossible under an illuminant having a spectral distribution different from that used in establishing the original

matches. It is well known, for example, that many materials do not look the same when viewed under illumination by sunlight and by light from an incandescent tungsten filament.

Furthermore, dichromism in solutions or glasses may complicate the problem of using standards different from the unknown. Thus, brom phenol blue exhibits different hues in different thicknesses. Corresponding inorganic standards, consisting of mixtures of solutions of colored salts, would probably not show this phenomenon. In such cases, the original matching thickness must be used.

For visual comparison, it is probably best to work in a booth fitted for maintaining reproducible conditions of illumination.

Standard series technic. The standard series technic includes some of the simplest procedures known in quantitative analysis. Beginning students in chemistry learn to use test papers that, when moistened with a solution, show the solution's approximate *p*H on comparison with a standard paper. This standard has printed on it the hues of an appropriate indicator at suitable *p*H intervals through the range of the color change.

Many variations of the standard series arrangement have been used. They vary from the crude means just mentioned to instruments equipped with cells of optical glass. Two examples will suffice to indicate some degree of refinement.

To hold solutions various forms of containers are used. For small thicknesses, such as 1 to 2 cm, test tubes or French square bottles of uniform thickness are suitable for horizontal observation. Greater thicknesses may be observed best in Nessler tubes, made preferably with

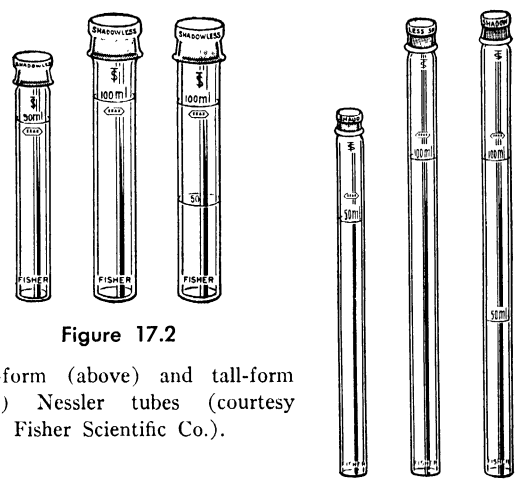


Figure 17.2

Short-form (above) and tall-form (right) Nessler tubes (courtesy Fisher Scientific Co.).

fused-on, plane glass bottoms. The latest design has a ground glass cover that remains in place for viewing. Various depths of Nessler tubes are available, in tall or short forms, graduated either for a particular volume or with many marks like a buret. Graduated lengths of 24 or 30 cm, holding 50 or 100 ml, are usually the most convenient long form. Figure 17.2 illustrates two forms.

To match the unknown against the standard the analyst may simply hold the two tubes side by side and look through them, preferably against some white background to reflect light through the tubes. Optical aids of various kinds increase precision and convenience. Also to facilitate comparison of tubes, a device that provides for moving the series of standards past the tube containing the unknown may be used. One of the common types of such devices is shown in Figure 17.3.

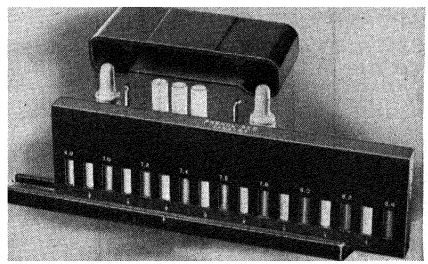


Figure 17.3

Slide comparator with solutions as standards (courtesy W. A. Taylor and Co.).

Vertical comparison of standard series of solutions provides for viewing greater thicknesses. It is usually done in tubes of the Nessler design. A mirror in the bottom of a holding rack reflects light up through the tubes. The unknown and standards are compared by placing them adjacent to each other and looking vertically down through them. In a more convenient modification, the unknown is fixed in position and the series of standards in a roulette rack is rotated until a matching pair is found.

Since one uses a given thickness or depth of solution when employing the standard series technic, the question of possible nonconformity of the system to Beer's law is of no concern. If standards other than solutions are used, nonconformity of the unknown solution to Beer's law must presumably be provided for in establishing the standards.

Balancing technic. Another widely used method of colorimetry consists in comparing the unknown solution with a single standard solution, the depth of one being fixed and that of the other changed until a color match is obtained. If the system conforms to Beer's law, the concentra-

tions of the desired constituent(s) in the two solutions are inversely proportional to the depths of solution measured. Stated in mathematical form,

$$b_1c_1 = b_2c_2$$

where b and c represent, respectively, depth and concentration in cells

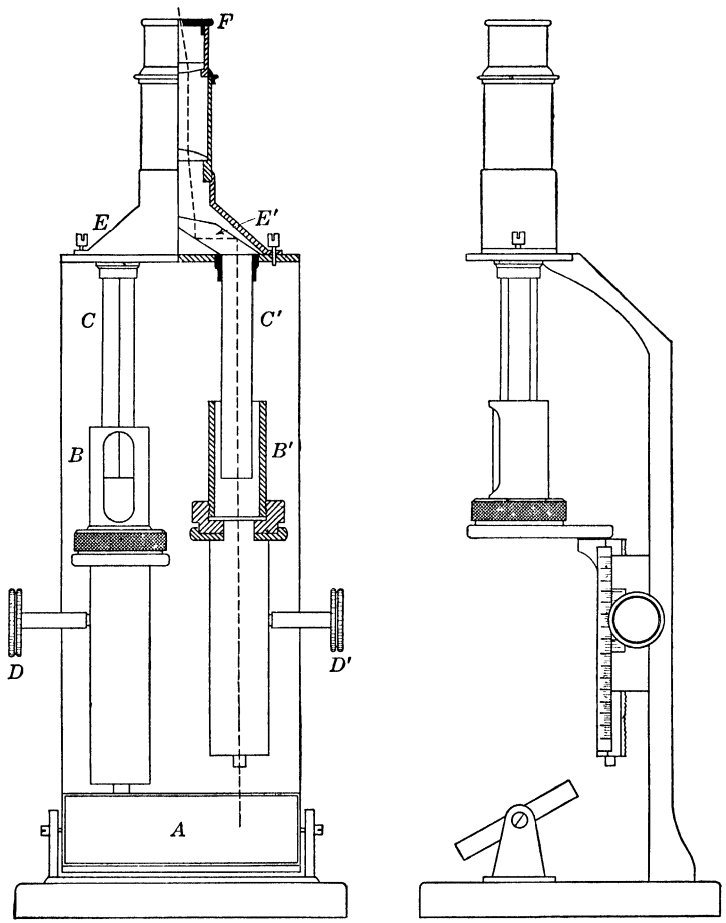


Figure 17.4

Diagram of Duboscq comparator. *A*, a mirror for directing light up through the cups; *B* and *B'*, glass-bottom cups for the known and unknown solutions; *C* and *C'*, glass prisms around which the cups can be raised by means of rack and pinions; *D* and *D'*, knobs to turn to change the depth of solution through which the light passes; *E* and *E'*, prisms for bringing the light beams together in a divided field in the eye piece *F*.

1 and 2. Knowing the depths, b_1 and b_2, in the two containers, and the concentration, c_1, of the standard, one may calculate the concentration, c_2.

$$c_2 = b_1c_1/b_2$$

When the two solutions do not conform to Beer's law, the standard and unknown must have nearly the same concentration, or a correction must be applied as obtained from an experimentally determined calibration curve.[14]

In its simplest form this technic requires only two similar, graduated cylinders. If Nessler tubes are used, the known solution may be put in one of them and then the unknown added to the other until the two match when observed vertically over a suitable reflecting surface. The concentration in the unknown may then be calculated from the volumes or depths read. Hehner cylinders, or the Schreiner or Campbell-Hurley comparimeters represent types of refinement of this technic.

The best-known instrument for making comparisons by balancing is that of Duboscq. Its principle is said to have been announced in 1854. Figure 17.4 illustrates the arrangement of the essential parts.

The measurement is made by filling one of the cups half full with the unknown solution and putting into the other cup about the same amount of a solution of known content similarly prepared, or a solution to be used as visually equivalent to the unknown (a permanent standard of different composition). The prism in the known solution is set at a definite depth, and the height of the cup containing the unknown is then adjusted up and down until a match is obtained. The concentration in the unknown equals that in the known multiplied by the factor, depth of known/depth of unknown.

Photometers

In contrast to comparimeters, color photometers are designed to measure the light-absorptive capacity of the system. In essence, the analyst really determines the I_o and I values previously discussed. Use of such instruments is based on the fact that the proportion of the incident light absorbed by a solution depends upon the amount of the absorbing material present. In order to calculate the concentration of the desired constituent from the transmittancy T_s of the solution, one employs the relationship expressed in the Bouguer-Beer law.

In order to understand the application of photometers, the student should be aware of certain well-known facts of physics, to be reviewed now. Of primary concern are the illuminant, the colored solution, and

[14] See Yoe, *Colorimetry*, Ch. 4, Wiley, 1928.

the detector for the transmitted light. Detectors are the human eye in visual instruments, and a photocell in photocell instruments.

Illuminants. Only rarely is sunlight used as the illuminant for a photometer. Occasionally the source may be a monochromatic radiator, such as the mercury arc, which provides a choice of several spectral lines, the strongest in the visual region being that at 546 mμ. Very generally, however, the source is an electric light bulb with an incandescent tungsten filament. The relative spectral distribution of the radiant energy emitted at different wavelengths by such a source at 3000°K, is shown by curve *A*, Figure 17.5. If only the two bands, 400 to 420 mμ and

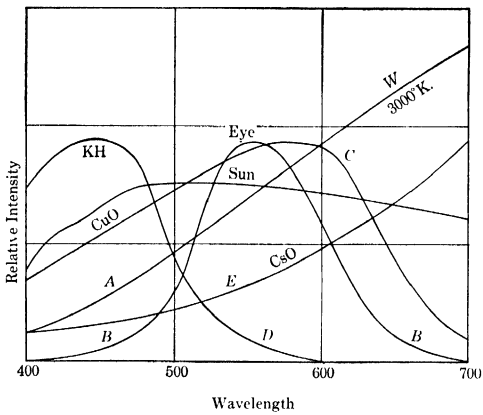


Figure 17.5

Relative intensity of energy emission and response.

680 to 700 mμ, were allowed to pass, their intensities would obviously be quite different. Such a limited range of wavelengths is known as a *spectral band;* the actual range, or *band width,* is specified in millimicrons.

Detectors. The two common detectors, the human eye and photocells, have response characteristics that vary widely for different wavelengths of radiant energy, or colors, as shown roughly in Figure 17.5. Curve *B* shows that the normal human eye is most sensitive to wavelengths just above 550 mμ, and that it is relatively insensitive below 430 mμ or above 680 mμ. This relative visibility curve is displaced at least 10 mμ to the left for the dark-adapted eye.

Users of visual instruments must beware of possible high percentage errors when matching in the far blue or red regions of the spectrum. The use of such instruments may also involve a serious fatigue of the observer in shifting back and forth from the dark-adapted state, required for photometric matching, to the light-adapted state, used for reading instrument scales.

Photocells of different types, or even of the same type, have a variety of response characteristics depending upon the materials and the methods of production used. Curves *C*, *D*, and *E* of Figure 17.5 illustrate responses of three types of photocells. Curve *C* is for the photovoltaic or photronic type, exemplified by those with a copper oxide coating. The relative sensitivity for different wavelengths of this cell roughly parallels that of the eye above 550 mμ, but below this point the cell is better. Even so, with this type of cell, one cannot expect the same instrumental response in the far blue as in the yellow-green. Many instruments use such cells. The current generated is sufficient so that amplification is not necessary for instrumental response.

The photoemission type of cell has different response peaks, depending upon the cathode coating. Curve *D* of Figure 17.5 is for a potassium hydride cell, and curve *E* for a cesium oxide cell. To have high sensitivity over a wide range of wavelengths, an instrument using such cells would require more than one cell. This necessity is recognized in the Beckman quartz spectrophotometer (see later description) which is equipped with two cells of quite different, but overlapping, ranges, so that whichever cell is more appropriate for the system to be measured may be used.

This type of photocell gives such a small response that the current has to be amplified for measurement. Consequently, instruments so equipped are more complicated than those using photovoltaic cells.

Occasionally, a photoconductive cell of the selenium type is used.

Photocells of different types have been incorporated in instruments in a variety of ways. Without going into detail, all that can be stated is that no one instrument seems to possess all the merits, and that they are not all equally satisfactory for all purposes.

Types of instruments. The variety and number of photometers that have been described and commercialized precludes anything more than mention of enough detail to illustrate certain principles. Some photometers are visual, but more are photoelectric. Some use one photocell, some two. This cell may be the photoemission type; more likely it is the photovoltaic type, especially in the less expensive instruments. Most spectrophotometers are the single-beam type, and most of them are not recording. In spectrophotometers prisms or gratings may serve as dispersing media for the illuminant. From all these instruments, two have been selected for brief description. They illustrate the various instrumental possibilities.

1. Filter photometers. Filter photometers are distinguished by their use of a filter, usually of glass, to isolate and pass a band of light in the

spectral region desired. Figure 17.6 shows the transmittance curves for five such filters.

The instrument illustrated [15] in Figure 17.7 is characterized primarily by the following points: (1) inexpensiveness; (2) small number of regular filters (more could be used); (3) two photovoltaic cells; (4) direct

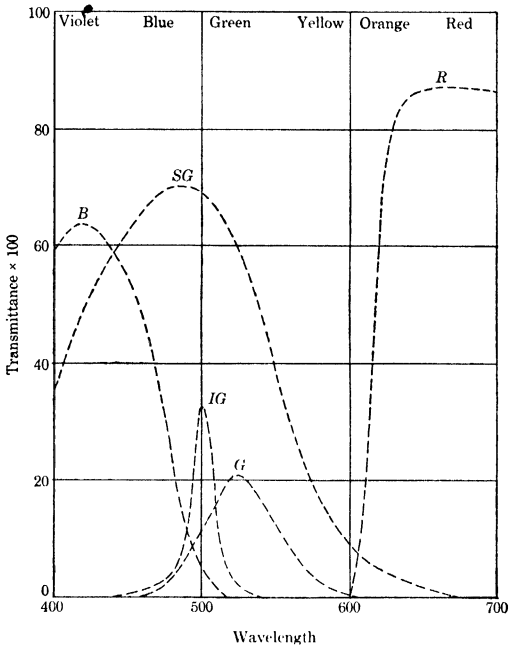


Figure 17.6

Transmittance curves for glass filters. Curves *B*, *G*, and *R*, respectively, are for the blue, green, and red filters regularly supplied with the Fisher photometer. Curve *SG* is for Corning signal green glass No. 440. The ordinate values show the percentage of the incident light passed at any given wavelength. It is evident that all these glasses pass relatively wide beams of light. Some composite filters, consisting of two or more glasses, pass narrower bands. A still narrower band may be isolated by an interference-type filter; curve *IG* represents one in the green region.

reading scales, in terms of transmittance and absorbance; and (5) variety of absorption cells available for different purposes. Directions for operating the instrument, including the establishment of a calibration curve for a specific desired constituent, are given in Chapter 29. Figure 17.8 shows a schematic diagram of the electrical and optical parts of this photometer.

[15] In a later model accessories provide for nephelometric and fluorescimetric measurements.

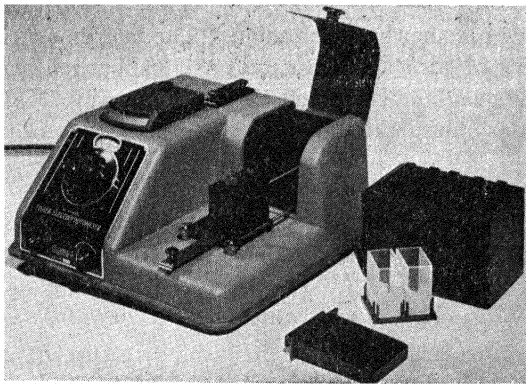


Figure 17.7

Fisher filter photometer (courtesy Fisher Scientific Co.).

Presumably, any method operable with a comparimeter may be adapted to a filter photometer. Since the perfection of the photocell, there has been an amazing changeover to the use of filter photometers. Although such instruments have become very popular, many standard series arrangements are entirely satisfactory for various kinds of work. The photoelectric photometers do, however, avoid the subjective uncertainty inherent in any visual method.

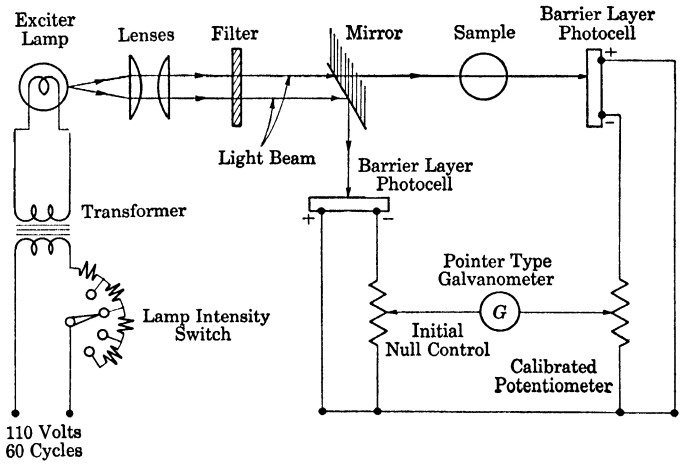


Figure 17.8

Schematic diagram of Fisher filter photometer (courtesy Fisher Scientific Co.).

The widely advertised freedom of photometers from the necessity of using standards is somewhat misleading. The instruments must be calibrated in terms of such standards, and this calibration should be done under working conditions and checked occasionally. Only the uninformed or the lazy put unquestioning confidence in unchecked meter readings.

Some instruments are made with precalibrated scales, one for each of a number of constituents. In use, the scale for the desired constituent is placed in position and the constituent read directly or from an accompanying table. This does not mean, however, that one or more of the scales should not be checked for reliability.

2. Spectrophotometers. The distinguishing feature of a spectrophotometer, as compared with a filter photometer, is the use of a monochromator for the isolation of the desired spectral band of light. Although the word "monochromator" implies light of a single wavelength, this result is not achieved unless the source is monochromatic. Actually a band of light is passed, the width varying from close to 1 A to about 35 mμ, depending on the instrument. In general, this band can be selected equally easily in any region of the spectrum.

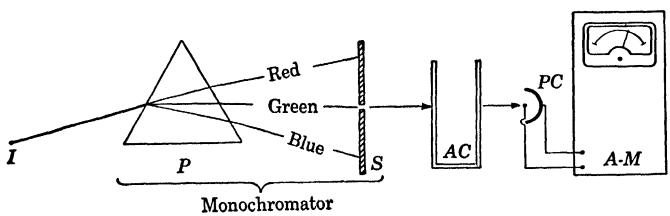


Figure 17.9

Elements of a spectrophotometer. *I*, illuminant; *P*, dispersing prism; *S*, slit; *AC*, absorption cell for a solution; *PC*, photoemission cell; *A-M*, combined amplifier and measuring meter. The small opening of the slit represents the portion of spectrum allowed to pass. Different portions of the spectrum may be isolated by rotation of the prism in order to bring the desired band of light to the slit opening.

Figure 17.9 shows the arrangement of fundamental components of a photoelectric spectrophotometer. Illustrative of this type of equipment, the Beckman Model DU spectrophotometer is a popular, high-grade commercial instrument with prismatic dispersion. Figure 17.10 shows the external appearance of the instrument, and Figure 17.11 shows the general schematic arrangement of the parts.

The Littrow mounting of the prism is familiar in spectrographs. The

quartz prism makes measurements possible over the range 200 to 1000+ mμ with photocells now available. Covering of even this range requires two photocells, one red-sensitive and one blue-sensitive (see Figure 17.5). The photometric scale is graduated in both transmittance and absorbance (optical density). High response sensitivity makes operation feasible with a slit so narrow that the band width usually approaches 1 mμ except

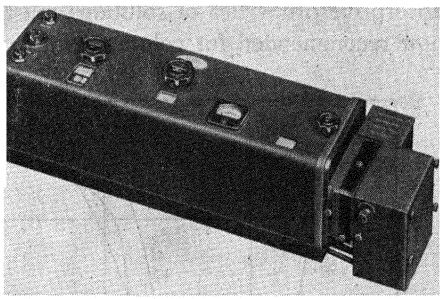


Figure 17.10

Beckman quartz spectrophotometer (courtesy Beckman Instruments, Inc.).

in extreme cases. Since adjustment of this slit is necessary to give a certain energy response, the band width is generally different for each wavelength setting. Consequently, one cannot ordinarily state that the values for a given curve are all for a given band width. Accessory attachments provide for a variety of measurements, including now a mechanical operator.

A newer Beckman instrument, Model B, embodies a system of glass

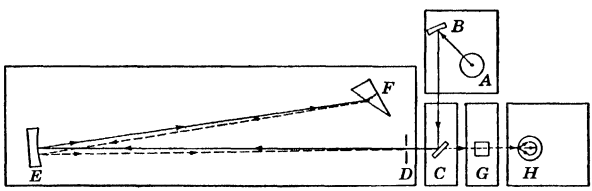


Figure 17.11

Schematic diagram of the optical system of the Beckman DU spectrophotometer. An image of the light source *A* is focused by the condensing mirror *B* and the diagonal mirror *C* on the entrance slit at *D*. The entrance slit is the lower of the two slits placed vertically over each other. Light falling on the collimating mirror *E* is rendered parallel and reflected toward the quartz prism *F*. The back surface of the prism is aluminized so that light refracted at the first surface is reflected back through the prism, undergoing further refraction as it emerges from the prism. The collimating mirror focuses the spectrum in the plane of the slit *D*, and light of the wavelength for which the prism is set passes out of the monochromator through the exit (upper) slit, through the absorption cell *G* to the photocell *H*.

optics. This feature limits the spectral range to the region of radiant energy passed by glass, which for this instrument, is approximately 320 to 1000 mμ. The spectral band width is somewhat wider than that usually maintained with the DU model.

Use of Photometers

Before suggesting the appropriate use of such instruments, the light-absorptive properties of solutions must be considered. Certain systems now recommended for colorimetric measurement in water analysis have

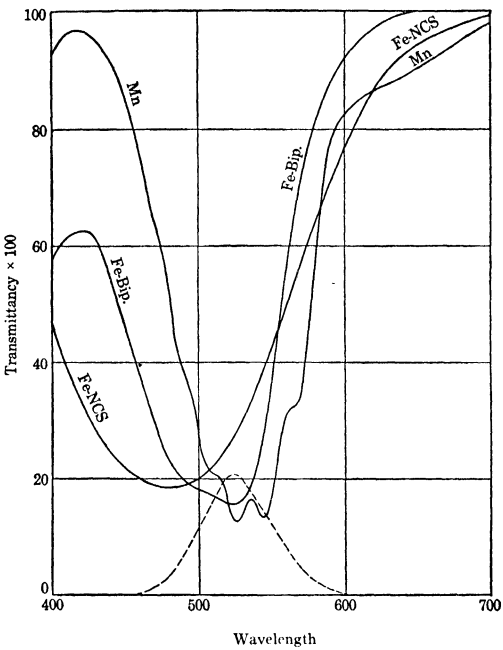


Figure 17.12

Spectral curves showing the use of a green filter for purple solutions. *Solid lines:* Mn, as permanganate; Fe-NCS, as iron thiocyanate; Fe-Bip., as iron-2,2′-bipyridine complex. *Broken line:* green glass filter.

been selected as examples.[16] Figures 17.12 and 17.13 show the spectral-transmittancy curves for some of these solutions. The percentage of light transmitted is plotted as the ordinate against the wavelength as the abscissa. The systems range in hue from yellow through reddish purple to blue. In Figure 17.12 the broken line represents the transmittance of a green glass filter. The solid lines represent the transmittancies of the following reddish-purple solutions: Mn as MnO_4^-; Fe^{+2} with 2,2′-bipyridine; and Fe^{+3} with SCN^-. In Figure 17.13 the broken lines represent the transmittances of blue and of red glass filters, and the solid lines the

[16] Mellon, *J. Am. Water Works Assoc.* **39**, 341 (1947).

transmittancies of the following solutions: Yellow, Cl_2 with o-tolidine; and NO_3^- with phenol-2,4-disulfonic acid; blue, Si and P as heteropoly blues.

As a general principle, it is desirable in quantitative determinations to measure the light-absorptive capacity at the wavelength of maximum absorptance (minimum transmittance) of the solution. In this region lies the greatest difference in transmittancy between any two different concentrations, as shown in Figure 17.14. This means maximum sensitivity

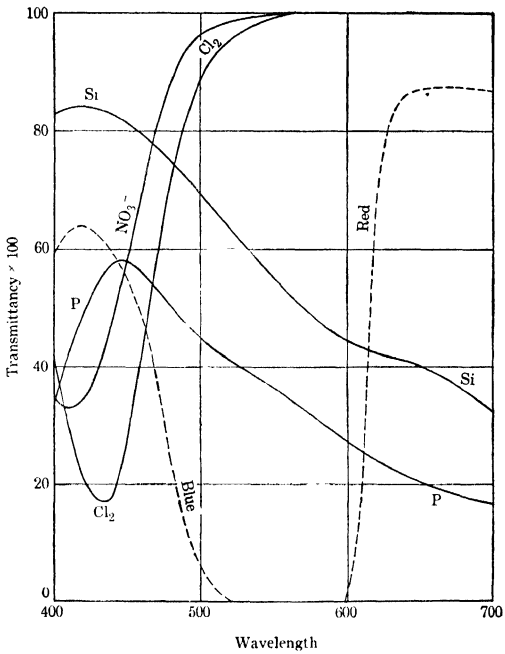


Figure 17.13

Spectral curves showing the use of a blue filter for yellow solutions and a red filter for blue solutions.

for the measurement. With this requirement in mind, the instrument is set to pass a light beam of the desired wave band. The three curves in Figure 17.12 all show minima, but those in Figure 17.13 do not, except for chlorine and nitrate. If there is no minimum, the only possibility is to work in the best region available. In some special cases, e.g., to avoid an interfering color, measurement cannot be made at the minimum point.

As already stated, the desired spectral band may be isolated by means of filters or a monochromator. This isolation involves both the width

of the band and its location in terms of wavelength. To illustrate the problem of selection, reference may be made to Figure 17.14. The solid-line curves are for a series of solutions of iron, ranging in concentration from 0.1 to 6.0 p.p.m., and consisting of the complex of iron with 1,10-phenanthroline. The peak of the absorption band of the iron solutions is close to 508 mμ. The maximum transmittance for the Corning glass

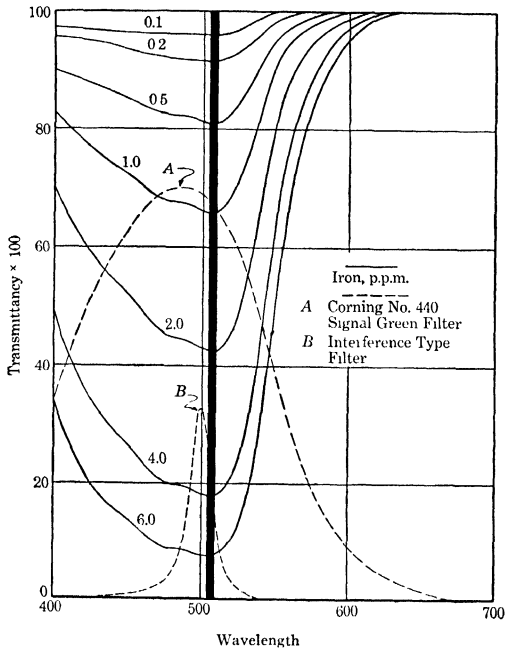


Figure 17.14

Spectral curves showing the use of two glass filters and a spectrophotometer for iron—1,10-phenanthroline solutions.

filter is near 485 mμ, and for the interference filter, it is near 500 mμ. Each is fairly close to the minimum value for the iron solutions; hence, either filter might be used. It should be noted, of course, that the spectral band passed by the Corning filter is wide; but most of the light is excluded above 550 mμ, where the high transmittancies of the iron solutions occur. The high selectivity of the interference-type filter is shown by its curve.

Preferably the selection of a filter for a given colored solution presupposes a knowledge of the transmittancy curve for the solution, as well as

the transmittance characteristics of the filters available. Referring again to Figures 17.12 and 17.13, one would select the green glass for the reddish-purple solutions, the red glass for the blue solutions, and the blue glass for the yellow solutions.

The wide line in Figure 17.14, centering on 508 mμ, represents[17] the band passed by a spectrophotometer set for 5 mμ. The versatility of the

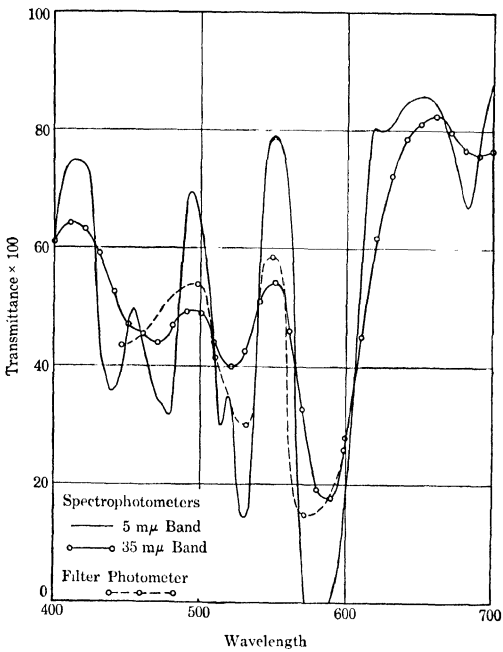


Figure 17.15

Spectral transmittance curves for didymium glass, using two spectrophotometers and one filter photometer.

best spectrophotometers lies in the means provided for obtaining narrow spectral bands and for locating them at any desired wavelength. One very selective assembled instrument has been described by Zscheile.[18] In fact, work with this instrument, as described by Comar and Zscheile,[19] is one of the excellent examples of the nearly unique usefulness of a good

[17] To emphasize the band width, this drawing shows the 5 mμ band as a uniform width throughout. Actually, it is triangular, narrow at the top and wide at the bottom, with the mid-height width 5 mμ.

[18] Zscheile, *J. Phys. and Colloid Chem.* **51**, 903 (1947).

[19] Comar and Zscheile, *Plant Physiol.* **17**, 198 (1942).

spectrophotometer for determining constituents in polycomponent colored systems.

Photometric data. Photometric measurement yields anything from a single transmittance (or absorbance) value at a single wavelength (or wavelength region) to a curve for a series of wavelengths. Such a curve is known as a spectral transmission (absorption, if absorptance is measured) curve. Figure 17.15 contains typical examples that show, for different wavelengths, the transmittance of a Corning didymium glass filter.

To determine such a curve, the analyst sets the instrument to pass a given wavelength region by means of filters or a monochromator. Then the ratio of transmitted to incident light is measured. This operation is repeated for the number of points desired.

The fact that Figure 17.15 shows three quite different curves for a single glass needs further comment. There are two general interpretations. First, plotting points taken at wavelength intervals too far apart will cause increased flattening of the curve as the points decrease in number, especially for materials having marked absorption bands, such as this glass. Second, using spectral bands too wide similarly smooths out an irregular curve. In Figure 17.15, the latter interpretation applies. The continuous curve, without points, was recorded with a band of 5 mμ, whereas that with the marked points was based on readings with a band of 35 mμ. The discontinuous curve was drawn through points marking the values obtained on a visual photometer with glass filters whose median wavelengths were given as the values locating the points on the graph. The disagreement of the three curves is obvious. Each curve *is* the curve for the glass, for the specific instrumental conditions used.

Calibration data. Once the filter photometer or spectrophotometer appropriate for the system to be measured has been selected, the light-absorptive capacity of the desired constituent in known amount must be determined. That is, the instrument must be calibrated under working conditions, such factors being involved as the filter or monochromator setting, the absorption cell, and any interfering constituents necessitating control.

Only two common uses of photometric data are considered here. In the first, a calibration curve is constructed co-ordinating the instrumental reading as the ordinate, to the concentration as the abscissa. In Figure 17.16 three possibilities are illustrated for the iron solutions of Figure 17.14. The solid-line curve is for transmittancy, as taken from a direct-reading spectrophotometer at 508 mμ. The broken lines are for logarithmic values. The one passing through 100 is plotted on the logarithmic

ordinate scale (plotting $\log_{10} T_s$ on a linear scale gives the same result). The one passing through zero uses $\log_{10} 1/T_s$. Many instruments read directly in the latter, or absorbancy values. However, the values are plotted, construction of such a curve involves determining them for a series of solutions of known concentrations under the conditions to be used later.

Another method of plotting calibration curves, illustrated in Figure 17.17, uses the transmittancy values of Figure 17.14 on a linear scale with

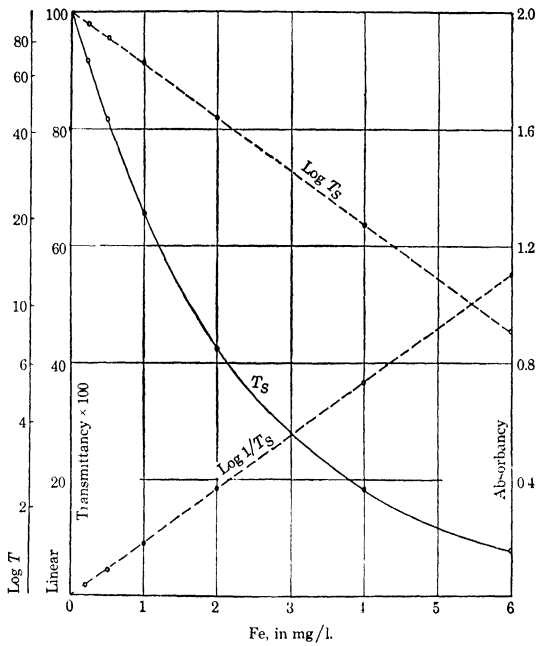


Figure 17.16

Three methods of plotting calibration curves.

concentration on a logarithmic scale. Ringbom[20] used absorptancy values ($100 - \%T_s$) in his original proposal of the method, and such a curve is included in Figure 17.17 as the broken line. Reference to the transmittancy curve shows a reasonably straight portion for the approximate concentration range of 1 to 4 mg/liter. This is the general region where, for a given photometric error, there is the least error in determining concentration.

[20] *Z. anal. Chem.* **115**, 332 (1939); see also Ayres, *Anal. Chem.* **21**, 652 (1949).

It may be pointed out that this method of plotting emphasizes the importance of avoiding, insofar as possible, calculations based upon very high or very low transmittancy values. The actual optimum transmittancy value varies with instrumental conditions. However, it is generally desirable, from this standpoint, to adjust operating conditions so that the measured transmittancy lies between 20 and 60 per cent. This result may be achieved in several ways, the following being feasible: (1) varying the amount of sample; (2) aliquoting the solution of the sample; (3) varying the cell thickness; and (4) using a suitable wavelength band for the illuminant. All of these adjustments mean simply that one takes into account the different items involved in the Bouguer-Beer law.

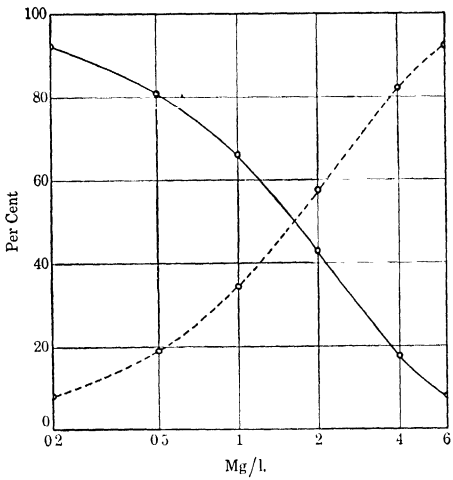


Figure 17.17

Curves co-ordinating transmittancy (solid line) and absorptancy (broken line) with concentration.

The linearity of the broken-line curves of Figure 17.16 show conformity of the system to Beer's law. For such systems the Bouguer-Beer relationship

$$c = \frac{\log_{10} 1/T_s}{a_M b}$$

may be applied without a calibration curve, c being the concentration of desired constituent in moles per liter, T_s the transmittancy, b the cell thickness, and a_M the molar absorbancy index for the given cell (usually defined for 1.000 cm). The value of $1/T_s$ is determined experimentally, b is known, and a_M must be determined for a solution of known concentration.

Applying this procedure to the determination of iron (Figure 17.14, curve for 4 p.p.m.), the transmittancy is 0.18 (18 per cent) at wave-

length 508 mμ. Since the concentration may be taken as 4 mg per liter (0.0000716 moles) and the cell thickness is 1.000 cm, the constant a_M is 10,400 for the curve determined at a band width of 10 mμ. This value may then be used for the system, under the conditions specified.

APPLICATIONS

Although the first color-forming reagent is said to have been mentioned by Pliny in about 60 A.D., colorimetric methods definitely came on the scene about 1850.[21] Progress was slow for another half-century, but since 1900 new color-forming reactions and new instruments for measuring colored systems have been appearing at a steadily increasing rate.

The situation has so changed, especially since 1940, that it seems safe to state that today colorimetric measurements are substantially on a par with gravimetric and titrimetric methods in practical importance. Some evidence for such a conclusion is shown in Table 17.1, which contains data for papers published during two different periods in *Analytical Chemistry*.

TABLE 17.1

SUBJECTS OF ARTICLES PUBLISHED IN ONE PERIODICAL
(in per cent)

Kind of Method	*1929-30*	*1950-51*
Colorimetric	11.1	24.4
Gravimetric	18.7	7.3
Titrimetric	30.8	27.0

The constituents determinable by colorimetry are both varied in nature and large in number. The new edition of the four-volume treatise by Snell and Snell [22] is the best cross-sectional sampling of the application of this method to inorganic and organic constituents. Current applications are so important that at least a dozen different single volumes have appeared. Some are general in nature, but others are specialized. As examples of the latter, Sandell's[23] book contains selected methods for the metals; Haywood and Wood's[24] smaller work contains composite procedures for all of the minor elements in each of a number of alloys; and Fister's[25] and Mehl's[26] collections cover important spectrophotometric

[21] Mellon, *Anal. Chem.* **24**, 924 (1952).
[22] *Colorimetric Methods of Analysis*, Van Nostrand, 1948-54.
[23] *Colorimetric Determination of Traces of Metals*, Interscience, 1950.
[24] *Metallurgical Analysis*, A. Hilger, 1944.
[25] *Manual of Standardized Procedures for Spectrophotometric Chemistry*, Standard Scientific Supply Co., 1950.
[26] *Manual of Clinical Procedures for Beckman Spectrophotometers*, Beckman Instruments, Inc., 1953.

methods for clinically important systems. The continuing advances in the field are evident in annual reviews.[27] A few typical examples of applications of colorimetric methods are given in the exercises in Chapter 29.

The wide applicability of this type of measurement has just been mentioned. As additional points of merit, the following items are important: (1) the speed, in many cases; (2) simplicity of the technic of measurement in most cases (including often the preparation of the system); (3) utility for extremely small amounts; and (4) variety of equipment available for making measurements. With the best spectrophotometers, colorimetry offers an almost unique approach for handling certain polycomponent systems.

Colorimetric methods have long been thought of as limited to low percentage ranges of constituents. An interesting development is the extension of this range to include at least certain constituents that are major components in materials. Hiskey[28] has developed the theory for this application, and Bastian's[29] papers report results obtained on certain industrial materials.

The accuracy of such methods varies widely. Some visual comparimetric results are probably no closer than 1 part in 20. Good spectrophotometers should approach 1 part in 100. The Hiskey-Bastian technic is said to approach good gravimetric or titrimetric work, that is, 1 part in 1000.

[27] Mellon, *Anal. Chem.* **21,** 3 (1949); **22,** 2 (1950); **23,** 2 (1951); **24,** 2 (1952); **26,** 2 (1954).
[28] Hiskey, *Anal. Chem.* **21,** 1440 (1949); **22,** 1464 (1950); **23,** 506, 1196 (1951).
[29] Bastian *et al., Anal. Chem.* **21,** 972 (1949); **22,** 160 (1950); **23,** 580 (1951).

CHAPTER 18

ELECTROMETRY

Certain properties of chemical systems may be translated by suitable apparatus into electrical effects. These effects can be used in a number of cases as an aid to chemical analysis. Methods employing electrical measurements are often called *electrometric methods*;[1] they may be used for three main purposes:

1. Determination of the concentration of a chemical species by relating the electrical measurement directly through some equation or method of calibration to the absolute concentration of the desired species. This type of technic is distinguished by the fact that the electrical quantity measured enters into the calculation of the amount of the desired constituent.

2. Indication of the equivalence point in a titration from the inflection points in the plotted, or otherwise noted, relationships of the electrical property measured *versus* the amount of titrant added. The electrical measurement is here actually used as a means of determining relative concentration change. Only the amount of titrant used, not the electrical values, enters into the calculation of the amount of the desired constituent present. The use of electrical methods in various types of titrimetric reactions was discussed in Chapters 13 to 15.

3. The obtaining of a record giving a composite qualitative and quantitative analysis of the sample. An example is a graph, the co-ordinates of which are the values of two different electrical properties, one of them related to the nature of the specific constituent being observed, and the other related to the amount of the constituent present. Polarography (discussed later in this chapter) is the only common electrical method that may be readily used for this purpose.

Electrical methods of the type indicated must be distinguished from

[1] See Chapter 30 for laboratory exercises.

electrodeposition (see Chapter 9) in which electrical effects are used as a means of separation rather than as a means of measurement. In such electrodepositions there is not 100 per cent current efficiency, that is, the ion reacting does not carry all the current. Consequently, the amount of constituent deposited cannot be calculated from the amount of current passed. It is well known, for instance, that the ammeter continues to read after all the copper is deposited (see method for copper in Chapter 28).[2]

Almost all of the commonly measurable electrical properties have been utilized for the first two purposes mentioned, that is, measurement of concentration and detection of equivalence points. A brief survey of available methods follows, the classification being by electrical property measured. Two methods are subsequently discussed in greater detail. The primary electrical variables that are readily measured are *potential* (volts), *current* (amperes, or coulombs per second), and *resistance* (ohms). The respective methods employed to measure these three properties are potentiometry, polarography, and conductometry. Other electrical variables include *capacity* (electrical storage of the material between the plates of a condenser, measured in farads and equal to the quotient of coulombs divided by volts); *dielectric constant* (equivalent to the ratio of the capacities of a condenser with the sample between its plates and with air between the plates); *magnetic susceptibility;* and *thermal conductivity.*

In the technics of coulometric analysis and coulometric titration the measurement may be based upon (1) the period of time a current of constant value is used to generate the titrant consumed in the reaction, or (2) the amount of electric current (number of coulombs) consumed in generation of the titrant.

CONDUCTOMETRY

Conductometric procedures involve measurement of the electrical resistance of solutions. The resistance is inversely proportional to the conductivity, which in turn is proportional to the number of ions present and to their mobilities. In simple dilute solutions the measured conductivity can be directly related to the concentration of ionizable substance present.

In a titration conductometric measurement can be used to follow the change in concentration. For example, in the titration of hydrochloric acid with sodium hydroxide the conductivity at first drops as sodium hydroxide is added, because of the effective replacement of the rapidly

[2] Lingane, *J. Am. Chem. Soc.* **67**, 1916 (1945), has described a method, called "coulometric analysis," in which the technic provides for obtaining 100 per cent current efficiency.

moving hydrogen ion by the much more slowly moving sodium ion. The conductivity reaches a minimum at the equivalence point, since the addition of excess sodium hydroxide then causes the conductivity to increase as a result of the increase in the number of ions. The measured conductivity is corrected for the dilution caused by added titrant.

Conductometric methods have a number of specialized applications, as in determining the salt content of "pure" or distilled water, following the rinsing of bottles after alkaline washing, and a very few titrimetric reactions involving neutralization, complexation, or precipitation.

The electrical apparatus used usually consists of a pair of platinum electrodes inserted into the sample, a Wheatstone bridge (one arm-resistance of which is usually the sample solution), a 1000-cycle source of potential, and a suitable current null-indicator, such as a galvanometer or amplifier and small cathode-ray (sector type) tube. Occasionally, a 60-cycle source is used.

The equipment employing high-frequency oscillator circuits can be used for essentially the same purpose as the older conductance measurement. Depending upon the type of electronic circuit used, the nature of the sample, and the type of sample cell employed, the measurement obtained with the high-frequency oscillator circuit may be primarily due to sample conductance, sample capacitance, or a composite of both. Such high-frequency oscillators usually operate in the megacycle frequency range.

Because of the limited use of conductometric methods, no procedures employing them are included in this book. Such procedures, as well as an extensive treatment of conductometry, are available in reference works.[3]

POTENTIOMETRY [4]

Potentiometric methods involve, essentially, measurement of the electrode potential of a half-cell system in the solution. For this purpose, it is necessary to insert into the sample solution an *indicator electrode*, that is, an electrode that will equilibrate itself with the chemical species, the concentration of which is to be determined, and which will therefore have a potential calculable on the basis of the Nernst equation for the

[3] Standard conductometry: Britton, "Conductometric Analysis," in Berl, ed., *Physical Methods in Chemical Anaylsis,* Academic, 1951; Britton, *Conductometric Analysis,* Van Nostrand, 1934, and *Hydrogen Ions,* Van Nostrand, 1943. High-frequency oscillators: Blaedel *et al., Anal. Chem.* **24,** 1240 (1952); Hall, *ibid.,* 1236 (1952); and Blake, *Conductometric Analysis at Radio-Frequency,* Chapman and Hall, 1950.

[4] General references: Bates, *Electrometric* p*H Determinations: Theory and Practice,* Wiley, 1954; Kolthoff and Furman, *Potentiometric Titrations,* Wiley, 1931; Kolthoff and Laitinen p*H and Electrotitrations,* Wiley, 1941; Laitinen, "Potentiometric Analysis," in Berl, *op. cit.* p. 105; and Lingane, *Electroanalytical Chemistry,* pp. 49, 68, 91, 105, Wiley, 1954.

particular species concerned. This potential is determined by reference to the fixed potential of a *reference electrode,* which is also in contact with the sample solution. The difference in potentials of the two electrodes is best determined by a device drawing effectively zero current, such as a potentiometer or a vacuum-tube voltmeter.

If the indicator electrode can be made specific enough in its action, concentration of a particular species can then be measured directly, as in the determination of *p*H or hydrogen ion concentration. Actually, it is important to remember that the indicator electrode responds to activities, and not to concentrations, of ions. In titrations, the indicator electrode usually responds to changes in concentration of the ion being titrated, the active ion of the titrant, or both.

In order to understand something of the mechanism involved in making potentiometric measurements, it is necessary to consider electrode potentials again. One aspect of this subject was considered in Chapter 9 in the discussion of separation by electrodeposition. In that discussion, the center of interest was to interpret the decomposition potentials of solutions subjected to electrolysis. In the present chapter we are interested in electrode potentials from the standpoint of their application in making quantitative measurements.

It has already been stated that the chemical elements can be arranged in an emf series on the basis of their characteristic standard electrode potentials, E^0. Also, according to the Nernst equation, the potential of an electrode consisting of an element in contact with a solution of its ions is given by the expression

$$E = E^0 - \frac{RT}{nF} \ln C$$

in which E is the measured potential in volts, E^0 the standard potential, R the gas law constant (8.313 joules/degree mole), T the absolute temperature, n the number of electrons lost in the half-cell equation as written, F the number of faradays, and ln C the natural logarithm of the concentration in moles per liter. Actually, the concentration can be expressed in moles per liter of solution only in the ideal case where the activity coefficient of the ion considered is unity. Use of concentrations for activities has been considered already and will be further discussed under the determination of *p*H values. When the appropriate values for R and F are substituted and the result multiplied by 2.303 to change from natural to Briggsian logarithms, the expression becomes

$$E = E^0 - \frac{0.0001983\ T}{n} \log C$$

At 25° the expression 0.0001983 T becomes 0.0591, which is used in subsequent discussion.

The foregoing equation expresses the potential of the half-cell reaction,

$$M \rightleftarrows M^{n+} + n\,e$$

where M^{n+} is the ion in equilibrium with a form of the element, M, itself. The latter is usually present as a solid, although it may be a gas or a liquid, of limited solubility in the solution. For half-cell reactions involving two oxidation states of the same element, as well as perhaps hydrogen or other ions, the Nernst equation can be used similarly to formulate the potential due to the species in solution.

From the equation given, it is evident that the value of C may be calculated if one knows E^0, and E is measured experimentally. The measurement of E, therefore, constitutes the essence of potentiometry. Such measurements may be made to determine the concentration of a solution as it stands, or to follow the change in concentration marking the course of some reaction, as in a titration.

Principle of Method

Since the E^0 value for hydrogen, in a solution having an activity of unity with respect to hydrogen ions, is taken arbitrarily as zero, the determination of hydrogen ions is probably the simplest case to consider, although the measurement itself is not necessarily the easiest to make experimentally. The basic method involves the measurement of the potential at equilibrium in the half-cell reaction

$$\tfrac{1}{2}\,H_2 \rightleftarrows H^+ + e$$

The electrode is platinum wire or foil, which, under suitable conditions, equilibrates itself with the system H^+/H_2. The standard hydrogen electrode potential of $E^0 = 0.0000$ volts is that of the above half-cell reaction at 25° for a solution of unit hydrogen ion activity, saturated with hydrogen gas and in contact with hydrogen maintained at 760 mm of mercury pressure.

In the arrangement illustrated in Figure 18.1 suppose the solution in container A is molar in hydrogen ions, that in container B is the unknown, and that the two are connected with a salt bridge. If hydrogen gas is bubbled through the two solutions to saturate the platinum electrodes (covered with platinum black), a definite potential will be established at each electrode, the magnitude of which will depend upon the hydrogen ion activity or concentration in the solution around the electrode. Consequently, there will be a definite potential difference between the two

electrodes, which can be measured by means of a potentiometer. Since the potential of the electrode in *A* is zero by definition, that of the other electrode is known at once. Then the observed potential is equal to $0 - 0.0591 \log [H^+]$ at 25° and 760 mm pressure.

In view of the practical difficulties of establishing and maintaining the standard hydrogen electrode, most measurements are based upon the use of some other reference system. In practice the calomel electrode, $Hg/Hg_2Cl_2/KCl$, is widely used on account of its ease of preparation and reproducibility. Careful measurements have established its relationship to the standard hydrogen electrode. Details regarding the preparation of, and values for, the calomel electrode are given later.

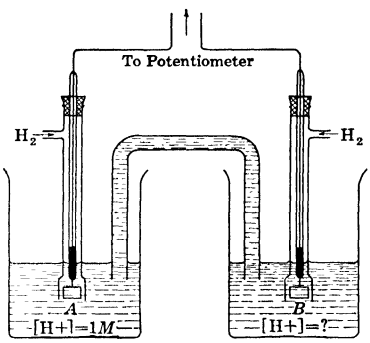


Figure 18.1

Arrangement of two hydrogen electrodes. *A*, molar in hydrogen ions; *B*, unknown.

A number of methods, employing various electrode combinations, have been proposed for the application of the potentiometric process to the measurement of concentration in different types of chemical systems. The principles of several of the methods are presented briefly in the subsequent discussion of apparatus and of specific procedures (see also Chapter 30, which contains several potentiometric procedures).

Apparatus

The apparatus necessary for potentiometric measurement, as previously mentioned, includes essentially only electrodes and means of determining potential differences. Only representative embodiments of commonly used types are described here.

Potentiometric determinations of the type described in this book require the use of two kinds of *electrodes*. One is a standard of reference, and the other is some system capable of responding to the ionic species to be measured.

Standard electrode. Since all procedures require the use of a standard reference electrode, the nature of that electrode will be described first. As stated already, the calomel electrode or half-cell is well suited for this purpose, although other systems have been used. The half-cell equation for the electrode reaction is

$$2\ Hg + 2\ Cl^- \rightleftarrows Hg_2Cl_2 + 2\ e$$

Since the calomel and the mercury are present as a solid, and as a liquid, respectively, and therefore are of constant activity, the Nernst equation for the half-cell equilibrium at 25° is

$$E = E^0 - 0.0591 \log \frac{1}{[Cl^-]}$$

Consequently, if the concentration of chloride ion is fixed, the potential of the system is determined. The values for three commonly used concentrations of potassium chloride solution at a temperature of t are

$$0.1M \text{ KCl}: \quad E = -0.3355 + 0.00006(t - 25)$$
$$1.0M \text{ KCl}: \quad E = -0.2831 + 0.00024(t - 25)$$
$$\text{Saturated KCl}: \quad E = -0.2443 + 0.00065(t - 25)$$

The Ag/AgCl system can be analogously used as a reference electrode system, as can the Hg/Hg_2SO_4 system.

As a container for the electrode materials one may use various designs of vessels, one of which is illustrated in Figure 18.2.

Indicator electrodes. An indicator electrode, as discussed previously, is one that will rapidly equilibrate itself with the species the concentration of which is to be measured. In neutralization titrations and *p*H measurement, the most widely used indicator electrodes are the hydrogen and glass electrodes. The quinhydrone electrode is used less frequently now than formerly, although it is inexpensive and convenient. Since metal-metal oxide electrodes are seldom used in neutralimetric determinations today, they will not be discussed. The platinum electrode is the favorite for oxidation reduction titration, and the silver electrode is used in certain types of precipitation and complexation titrations. All of these types of electrodes (with the exception noted) will now be examined in some detail.

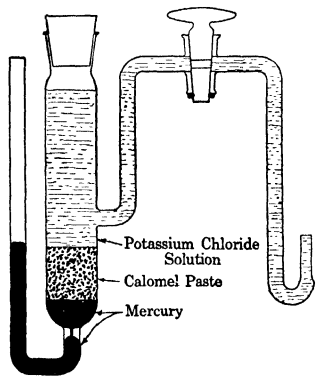


Figure 18.2

Calomel electrode vessel.

For general work the form of *hydrogen electrode* assembly illustrated in Figure 18.1 (page 280) is convenient. The electrode proper, consisting of a small rectangular piece of platinum or gold foil, is fastened to a wire sealed through the small glass tube. Mercury is placed inside the tube to provide electrical connection when a copper wire is inserted into the top of the tube. The foil should be coated with platinum black.

In some cases platinum electrodes are erratic and yield potentials of uncertain reliability. Whenever accurate values are desired, the electrode should be checked against a solution of known *p*H value. N.B.S. potassium hydrogen phthalate is recommended for this purpose. A 0.0500*M* solution has a *p*H of 4.005 ± 0.003 at 25°. Also some assurance of reliability can be obtained from the use of duplicate electrodes with electrical arrangements for measuring them alternately. Reference works should be consulted for conditions limiting the application of hydrogen electrodes.

In addition to Standard Sample No. 185 of potassium hydrogen phthalate[5] (*p*H 4) the National Bureau of Standards also has available for use as *p*H standards Standard Sample No. 186 (phosphates, *p*H 7) and Standard Sample No. 187 (borax, *p*H 9).

In determination of hydrogen ion concentration by measuring the potential between a hydrogen electrode and a standard calomel electrode, the observed value will be the difference between the potentials of the two electrodes. For the molar calomel half-cell, we have at 25°

$$\begin{aligned} E_{\text{observed}} &= E_{\text{H}^+/\text{H}_2} - E_{\text{cal}} \\ &= -0.0591 \log [\text{H}^+] + 0.283 \end{aligned}$$

$$\log [\text{H}^+] = \frac{0.283 - E_{\text{observed}}}{0.0591}$$

Since $p\text{H} = -\log[\text{H}^+]$

$$p\text{H} = \frac{E_{\text{observed}} - 0.283}{0.0591}$$

For a potentiometer graduated in millivolts, the potential reading in millivolts (*mv*) is related to the *p*H as follows:

$$p\text{H} = \frac{mv - 283}{59.1}$$

The so-called *quinhydrone electrode* actually involves a bright (unplatinized) platinum or gold electrode, similar to that used with a hydrogen electrode. In use, it is immersed in the solution to be measured; the latter is then saturated with quinhydrone, a molecular compound containing equimolecular proportions of quinone, $C_6H_4O_2$, and hydroquinone $C_6H_4(OH)_2$. The small amount necessary to saturate an aqueous solution is largely dissociated into the two compounds, along with hydrogen ions formed by dissociation of the hydroquinone. The equilibria may be represented by the equation

[5] See "Certificate for Standard Sample 185, Acid Potassium Phthalate (*p*H Standard)," Nat. Bur. Standards, 1945.

$$C_6H_4O_2 \cdot C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + C_6H_4(OH)_2$$
$$C_6H_4(OH)_2 \rightarrow C_6H_4O_2 + 2\ H^+ + 2\ e$$

At 25° the Nernst equation expressing the potential of a platinum electrode in equilibrium contact with the system is

$$E_{QH} = E^0_{QH} - \frac{0.0591}{2} \log \frac{[C_6H_4O_2][H^+]^2}{[C_6H_4(OH)^2]}$$

E^0_{QH} is the molar potential of the quinone-hydroquinone system. Since quinone and hydroquinone are present in equimolecular amounts, their activities can be assumed to be about equal and the ratio of their concentrations to be unity. Consequently, the above expression reduces to the form

$$E_{QH} = E^0_{QH} - 0.0591 \log [H^+]$$

Careful measurement has shown that the potential of the electrode reaction

$$\tfrac{1}{2}C_6H_4(OH)_2 \rightleftarrows \tfrac{1}{2}C_6H_4O_2 + H^+ + e$$

under standard conditions is more positive than the standard hydrogen electrode reaction, determined under comparable conditions, by 0.6992 volts at 25°. At this temperature, the above expression becomes

$$E_{QH} = -0.6992 - 0.0591 \log [H^+]$$

The value −0.6992 may be considered as the reduction potential of quinone in a solution with respect to hydrogen ions. The value at other temperatures may be calculated from the formula

$$E_t = -0.7177 + 0.00074\ t$$

where −0.7177 is the potential at 0° and t the temperature.

In practice, the potential difference between a quinhydrone and a standard or reference electrode is given by the expression,

$$E_{\text{observed}} = E_{\text{std.}} - E_{QH}$$

For the molar calomel electrode at 25° this becomes

$$E_{\text{observed}} = 0.6992 + 0.0591 \log [H^+] - 0.283$$
$$= 0.416 + 0.0591 \log [H^+]$$

Then

$$\log [H^+] = \frac{E_{\text{observed}} - 0.416}{0.0591}$$

If the pH is desired,

$$p\text{H} = \frac{0.416 - E_{\text{observed}}}{0.0591}$$

For a potentiometer graduated in millivolts,

$$p\text{H} = \frac{416 - mv}{59.1}$$

Among the advantages of the quinhydrone electrode are the facts that it (1) attains equilibrium quickly; (2) may often be used in solutions for which the hydrogen electrode is unsuitable, such as those containing oxidizing agents or salts of metals below hydrogen in the emf series; (3) is not so subject to "poisoning" as the hydrogen electrode; and (4) is simple to prepare.

The following disadvantages should be kept in mind: (1) solutions having a *p*H above 8 cannot be measured satisfactorily with this electrode, since some air oxidation of hydroquinone occurs; (2) some side reaction may alter the molecular ratio of quinone to hydroquinone and thus disturb the potential; (3) appreciable errors may occur in the presence of proteins or certain salts; and (4) the sample is contaminated with quinhydrone.

The polished platinum electrode used with quinhydrone should be thoroughly cleaned with chromic acid cleaning solution. About 1.1 g of quinhydrone is added to each 100 ml of solution to be tested and the solution is stirred well. The clean electrode is immersed in the solution and connection made to a reference calomel electrode by means of a salt bridge containing a saturated solution of potassium chloride. The emf of the system may be measured almost immediately.

Certain kinds of glass film function as a *glass electrode*.[6] If two solutions differing in *p*H are separated by such a membrane, which is permeable only to hydrogen and hydroxyl ions and water, a theoretical difference in potential between the two solutions is given, at 25°, by the relation

$$E = 0.0591 \log \frac{[H_1^+]}{[H_2^+]}$$

When properly made and used, the potential of the glass electrode varies as predicted. In general, the glass electrode (Figure 18.3) consists of a 0.1 *N* solution of hydrochloric acid in which an indicator Ag/AgCl electrode is immersed, the whole being enclosed in a glass sac. Special glass electrodes must be used in the alkaline region beyond *p*H 9 or 10, above which the salt content of the solution begins to affect the potential.

As a result of slight variations in the electrical characteristics of the thin glass, owing to manufacturing processes, glass electrodes may exhibit

[6] For further information on the theory and application of the glass electrode, see Dole, *The Glass Electrode*, Wiley, 1941, and also the book by Bates cited previously.

small differences in potential of the order of a few millivolts. Normal aging and slight chemical attack over a period of service may also affect the thin-wall glass membrane. This effect is known as the *asymmetry potential.* In precision *p*H meters an adjustment is provided to compensate for the effect in calibration with a buffer solution of known *p*H.

Compared with the hydrogen and the quinhydrone electrodes, the glass electrode has certain advantages for the determination of hydrogen ion. No chemical is added to the solution measured. The potential is independent of the presence of oxidation-reduction systems which affect potentials measured with a metal electrode. There is no interference by color, turbidity, or substances poisoning hydrogen electrodes. Unbuffered solutions can be measured and equilibrium is attained very quickly. Very small volumes (fractions of a milliliter) of sample solution will suffice, or the electrodes can equally well be immersed in large tanks or flowing streams.

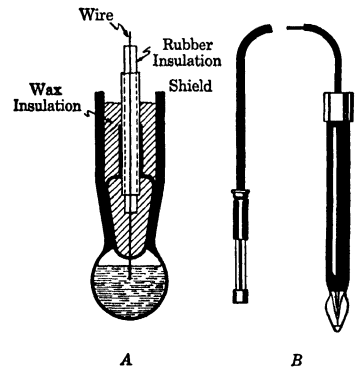


Figure 18.3

Commercial type of glass electrode, *B*; *A*, cross section (courtesy Beckman Instruments, Inc.).

As disadvantages, the following points may be noted. The high electrical resistance of even the thinnest glass film necessitates the use of a vacuum-tube amplifier in the balancing system or similar highly sensitive measuring equipment, but such vacuum-tube instruments are now readily available (see Figures 18.8 and 18.9 on page 289). The need to change electrodes at *p*H 9.5 has been mentioned. Excess alkali metal ions interfere, especially in the alkaline region and above *p*H 9, although there are glasses that minimize these sources of error. The fragile nature of the glass electrode is often a source of inconvenience. However, in spite of these difficulties, the glass electrode is now the overwhelming choice for the measurement of *p*H.

The *platinum electrode* serves for most measurements involving oxidation-reduction systems and reactions. A platinum wire sealed into a glass tube with a short exposed section of metal is satisfactory. It is used also as a part of the hydrogen and the quinhydrone electrodes for *p*H measurement.

A *silver electrode* consisting of a piece of exposed silver wire, silver rod, or platinum wire plated with silver, when electrolyzed as anode in a

dilute solution of hydrochloric acid, is transformed into a silver-silver chloride electrode. The silver or silver chloride electrode is widely used as an indicator electrode for silver ions, as well as for ions that form insoluble silver salts or stable silver complex species. It is satisfactory for the titration of halide ions with silver nitrate solution. It is used as the reference electrode portion of the glass electrode (Figure 18.3).

Many other *indicator electrodes* in addition to those described have been proposed for specific applications or more general uses. In any case, the indicator electrode must be capable of varying potential response with changing concentration of the constituent to be measured.

Measuring instruments. Although the main feature in the development of use of a potentiometric method is the selection of a suitable indicator electrode, the means used to measure the potential difference between indicator and reference electrodes is important.

For general, precise measurement of potential differences, a potentiometer is used. This involves balancing the emf resulting from the difference in potential of the indicator and reference electrodes with a known emf selected from a wire along which there is a uniform drop of potential.

With high resistance systems, such as that involving a glass electrode, a vacuum-tube voltmeter or potentiometer with electronic amplification in the balancing circuit is necessary. Figures 18.8 and 18.9 (page 289) illustrate typical commercially available instruments of the direct-reading and balancing types.

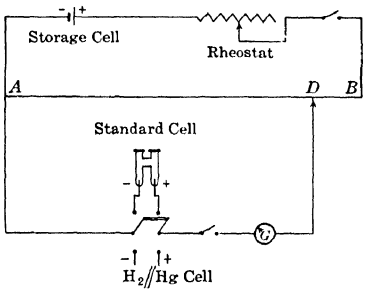


Figure 18.4

Circuit of simple potentiometer.

The essential parts of a simple potentiometer circuit are illustrated in Figure 18.4. The storage cell provides the working potential for the measurement. For constancy of potential a lead storage cell is preferable, although a simple dry cell will serve. The rheostat provides for total control of the drop in potential along the wire *AB*. The standard cell is one of known potential, as 1.0186 at 25° for the Weston cell, illustrated in Figure 18.5. The sample cell represents an electrode pair, such as the hydrogen-calomel cell, the potential difference of which is to be measured. Both the standard cell and the unknown cell are connected to oppose the potential of the storage cell. The double-pole,

double-throw switch enables either the standard or unknown cell to be put into the active circuit.

To make a measurement, the contact D in Figure 18.4 is set at B, the switch is thrown to put the standard cell in the circuit, and the rheostat

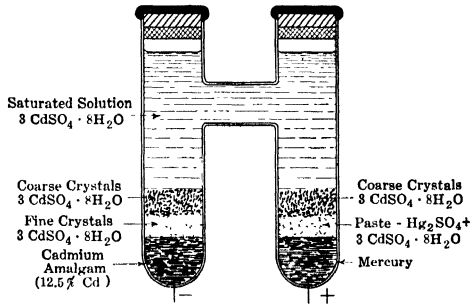


Figure 18.5

Weston standard cell (saturated).

is adjusted until the galvanometer shows no deflection when the tapping key is closed momentarily. The unknown cell is then substituted for the standard cell by throwing the switch the opposite direction, and the position of contact D is changed until the galvanometer shows no deflection when the circuit is closed by tapping the key. Since the potential in the "unknown" loop is now identical with the potential drop along AD in the reference loop, the potential of the sample cell is given by the relation

$$E_{\text{unknown}} = E_{\text{std.}} \times \frac{AD}{AB}$$

Where $E_{\text{std.}}$ is the potential of the standard cell employed.

In commercial potentiometers the unknown potential can be read directly from a scale. To achieve this result, the fall in potential per unit length of the wire AB is adjusted to some decimal fraction of a volt.

The slide wire AB is calibrated as follows: The contact D is set on AB such that the distance AD is numerically equal to the potential of the standard cell. For example, if the latter is 1.0186 volts, and if the slide wire AB is divided into, for example, 1700 divisions, starting with 0 at A, D is set at the point corresponding to 1018.6 divisions. When the rheostat is adjusted to zero galvanometer deflection, the fall in potential along AD is 1.0186 volts, or 1 millivolt per unit division.

For measurements in millivolts, the Leeds and Northrup student-type potentiometer is widely used. The internal wiring connections of the

potentiometer circuit are shown in Figure 18.6. The labels are explained in the operating directions inside the cover of the instrument. Figure 30.2 (page 542) shows the component items of equipment required for precise potential measurement and the necessary connections. The operation of the apparatus is described in Chapter 30.

Hildebrand [7] proposed a *millivoltmeter assembly,* illustrated in Figure 18.7, in which the potential is measured directly by means of a sensitive

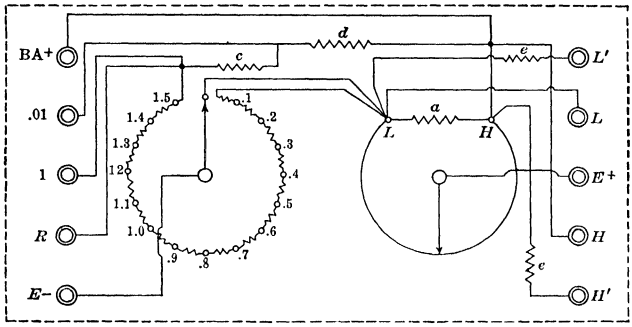


Figure 18.6

Internal wiring of student potentiometer.

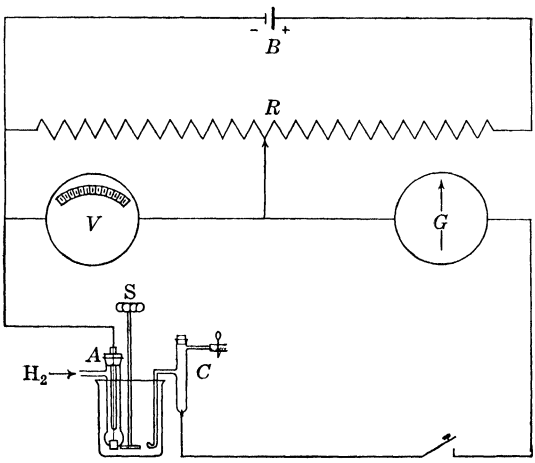


Figure 18.7

Hildebrand arrangement for potentiometric titrations. *B*, battery; *R*, resistance; *V*, voltmeter; *G*, galvanometer; *S*, stirrer; *A*, hydrogen electrode; H_2, hydrogen gas stream; *C*, calomel electrode.

[7] *J. Am. Chem. Soc.* **35**, 847 (1913).

meter. The apparatus is somewhat cheaper than the other assembly, as well as more rapid. Although the readings are less reliable than those of a potentiometer, they are satisfactory for use in plotting potentiometric titration curves.

As previously indicated, two types of *vacuum-tube pH meters* are available for potential measurement. They use electronic amplification to aid in securing the desired sensitivity under conditions of practically zero current flow. Usually the direct-reading instrument (Figure 18.8) is essentially a vacuum-tube millivoltmeter with the scale marked in *p*H



Figure 18.8

Coleman model A.C. *p*H electrometer (courtesy Coleman Instruments, Inc.).

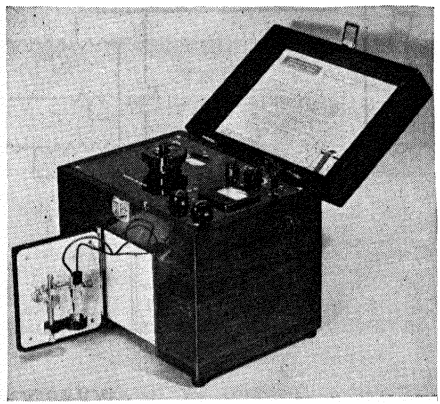


Figure 18.9

Beckman model G, precision type of *p*H meter, with glass electrode (courtesy Beckman Instruments, Inc.).

units and millivolts. The sensitivity is about ± 0.05 *p*H units, corresponding to 3 millivolts. The instrument illustrated is operated directly from the 110-volt A.C. line. Generally this type is less expensive than the balancing instruments.

Balancing instruments (Figure 18.9) usually require batteries for their operation; however, these batteries are compact and fit in the instrument. The instruments are basically potentiometers using electronic amplification in detecting the point of balance in the circuit. The sensitivity of the balancing instrument is usually better than 0.02 *p*H units. Figure 18.10 shows a diagram of the electrical circuit of one balancing instrument.

No further description of such instruments is included, as this kind of

information is available in the instructions furnished with each instrument.

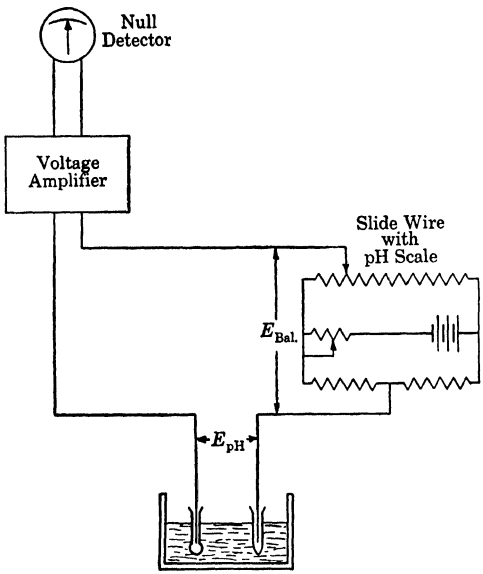


Figure 18.10

Electrical circuit of a vacuum tube *p*H meter.

POLAROGRAPHY [8]

The technic of polarography was announced in 1922 by Heyrovsky, and its development during the following 15 years was almost the exclusive work of this investigator and his colleagues. Since then, several thousand papers have been published on the technic, including its theoretical basis and varied applications.[9]

As applied in analytical chemistry, the technic is an electrochemical method in which current is measured [10] while a known potential is applied externally to a microelectrode immersed in the sample solution. A reference electrode is used as the basis of potential measurement.

The theoretical basis of polarography is more complicated than that of potentiometry, and no attempt is made here to develop it beyond a

[8] See Kolthoff and Lingane, *Polarography,* 2 vols., Interscience, 1952; Müller, *The Polarographic Method of Analysis,* Chemical Education Publishing Co., 1951; and Rulfs, "Polarographic Analysis," in Boltz, *Selected Topics in Modern Instrumental Analysis,* Prentice-Hall, 1952.

[9] See *Leeds and Northrup Bibliography of Polarographic Literature,* Leeds and Northrup, 1950, and *Proceedings of the First International Polarographic Congress,* Vol. II, 1951.

[10] Since current is the quantity measured, "polarography" is not a name consistent with such terms as "volumetric" and "electrometric."

minimum explanation. A good elementary introduction is given by Rulfs in the reference cited.

Principle of Method

Polarography combines electrolysis at definite applied electrode potentials with measurement of the current flow. The electrolysis is of short duration and is not carried on to any significant extent because of the use of a microelectrode immersed in a relatively large volume of solution. An unpolarizable electrode is used as the reference electrode so that any change in potential and current can be referred directly to the processes occurring at the microelectrode.

Electrode reactions occur which involve a transfer of electrons between the electrode and components of the solution. Since free electrons cannot exist in solution by themselves, any process of reduction at the cathode involves simultaneous oxidation at the anode. For example, if cadmium ion is being reduced in a chloride solution, the electrode reactions may be represented by the equations

$$\begin{aligned} &\text{Microelectrode:} && Cd^{+2} + 2\,e + Hg \rightarrow Cd(Hg) \\ &\text{Reference electrode:} && Hg + 2\,Cl^{-} \rightarrow Hg_2Cl_2 + 2\,e \end{aligned}$$

The solution must contain other electrolyte material in a concentration considerably greater than that of the substance to be electrolyzed in order to insure a high conductivity in the solution. Also this concentration insures that the limiting current which is measured is solely a diffusion current. It amounts to minimizing the contribution of the electroactive species to the ordinary migration current.

This *supporting* (or background) *electrolyte* is an indifferent salt that conducts the current but does not react with the substance under investigation, or at the electrode in the range of potential that is studied. That is, the ions of the added electrolyte do not produce a current increase by being reduced or oxidized at a potential before those at which current increases result from the ions for which the analysis is being made.

The procedure generally followed is to add a known amount of the sample solution to the supporting electrolyte, which contains the so-called "indifferent" electrolyte in concentration greater than 0.1 M. Typical indifferent electrolytes are potassium chloride and ammonia-ammonium chloride buffer. The sample solution is added in such amount as to bring the concentration of the sought ions into the range of 10^{-2} to 10^{-6} N. The supporting electrolyte must be present in a molar concentration of at least 50 and preferably 100 times that of the reducible species.

Figure 18.11 shows the fundamental electrical circuit used in polarographic measurements, which includes a potential source such as a 2-volt battery, a potentiometer, and a sensitive galvanometer. The sample cell has connected to it a reference electrode, such as a saturated calomel electrode, usually via an agar salt bridge. In many polarographic applications a satisfactory reference electrode is formed by a pool of mercury at the bottom of the sample beaker. The potential of such a reference electrode is determined by the nature and concentration of the anions in the sample solution. If the latter is 0.1 *M* in chloride ion, the pool potential will approximate that of the 0.1 *M* calomel electrode.

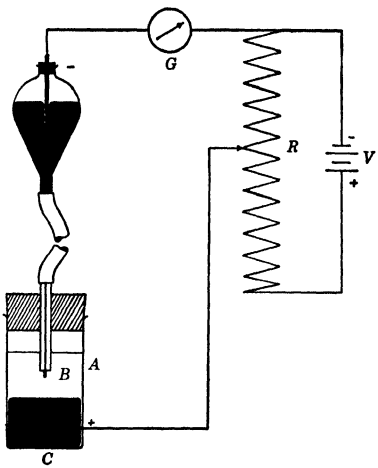


Figure 18.11

Electrical circuit of a polarograph. *V*, source of potential; *R*, potentiometer; *G*, galvanometer; *A*, sample cell; *B*, microelectrode; *C*, pool of mercury.

Dipping into the sample solution is the polarizable microelectrode, which usually is a capillary having an opening about 0.03 mm in diameter. From it a minute drop of mercury falls at regular intervals of 2 to 6 sec. The mercury must be forced through the capillary with a pressure of 40 to 60 cm of mercury. The microelectrode is said to be polarized, since it assumes whatever potential may be impressed upon it from an external source. The large reference electrode is nonpolarizable; that is, its potential is independent of the applied potential.

The polarizable microelectrode is the essential feature of the polarographic technic. In place of the dropping mercury electrode, a very small electrode of platinum wire may be used, although the former is preferred for most work.

Practice of the Method

The practice of polarography can be illustrated by considering a sample solution that is 0.1 *M* in potassium chloride and 10^{-3} *M* in cadium chloride. Oxygen from the dissolved air is removed by bubbling nitrogen through the solution for several minutes. During the measurement the surface of the solution is swept with nitrogen in order to exclude oxygen, since the latter is itself reducible at the microelectrode.

The potential applied to the microelectrode is then varied from 0 to about −2 volts by adjustment of the potentiometer. The current flow is noted as the potential is varied and a current-potential curve, such as that in Figure 18.12, is obtained. The potential applied to the indicator microelectrode is plotted as the abscissa and the current as the ordinate. The origin is fixed as the point at which the potential applied to the microelectrode is zero, thus representing the potential of the reference electrode used and at which the current flow is zero. The current may be in terms of scale divisions of a galvanometer or other current-recorder, or in microamperes if the current indicator has been so calibrated.

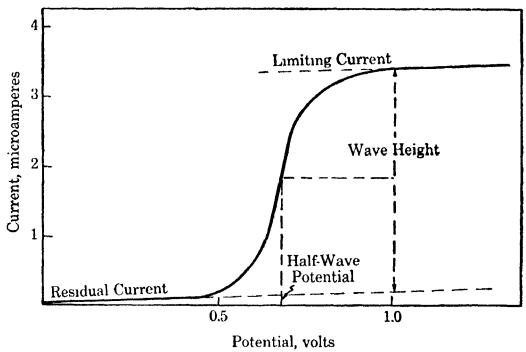


Figure 18.12

Current-potential curve.

Initially, on application of a very small potential, only an exceedingly small current, called the *residual current,* flows through the cell. When the decomposition potential of a reducible substance is reached (here the cadmium ion), the current flow increases as a result of continuous electrolysis. Further potential increase results in an *S*-shaped wave (see curve in Figure 18.12), since the current gradually approaches a limiting value, the *limiting current.* It finally becomes constant and relatively independent of further increase in the applied potential until the decomposition potential of another reducible species is reached, when the process repeats itself. Finally, the decomposition potential of the cation present in large amount (here potassium) is reached.

Under the proper conditions, and with all other factors kept constant, the height of the step or wave in the curve (determined according to the explanation in Chapter 30) is directly proportional to the concentration of the electroreducible substance producing it. The potential at the mid-

point of the wave, the *half-wave potential,* is characteristic of this substance for the particular solution composition involved. These two facts are then the basis of quantitative and qualitative polarographic analysis.

Although current-potential curves are readily obtained manually by observation of the current at a large number of different applied potentials, instruments are available that automatically vary the potential and record the current flow. The record is obtained by recording photographically the galvanometer-beam deflection or by the pen deflection of a strip-chart recorder as an inked track. Such a record is shown in

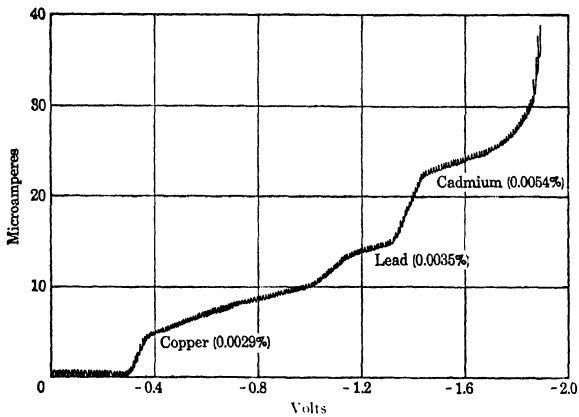


Figure 18.13

Polarogram of copper, lead, and cadmium in a high purity zinc-base die cast alloy.

Figure 18.13, which indicates the possibility of simultaneous qualitative and quantitative analysis under favorable conditions. Other means of recording are used.

The apparatus for potential variation and current measurement is generally called a *polarograph,* and the current-potential record a *polarogram.*

Fundamental Equations

Before the commencement of the polarographic wave, only a small residual current flows. It is usually considered to be a nonfaradayic or condenser current. In practical work this current is subtracted by the proper measurement of the wave height. When the decomposition potential of a species in the solution is reached, the concentration of this electroactive species at the electrode-solution interface decreases because

of removal of the species by electrolysis. This causes an increase in the rate of diffusion of these ions from the main body of the solution to the interface.

The current that flows is dependent upon the rate of diffusion of the reducible substance, which in turn is a function of the concentration gradient that results between its concentrations at the interface and in the bulk of the solution. For cathodic waves, that is, waves resulting from a reduction process at the indicator microelectrode, the *current flow* may be expressed by the equation

$$i = K(C_o - C)D^{1/2}$$

where $K = k\ n\ F\ m^{2/3}\ t^{1/6}$ (the terms are defined later); i is the current at any instant on the polarographic wave; C_o is the concentration of the species in the state as added, that is, the oxidized form in the main body of the solution; C its concentration at the electrode surface; and D its diffusion coefficient in the solution.

Since the concentration of the oxidized form of the species at the interface becomes zero as the applied potential is increased, the diffusion current then depends only upon the concentration of the reducible substance in the main body of the solution. Thus

$$i_d = K\ C_o\ D^{1/2}$$

This expression is known as the Ilkovic equation for the diffusion-controlled current.

For 25° the equation is

$$i_d = 607\ n\ D\ C\ m^{2/3}\ t^{1/6} \tag{18.1}$$

where i_d is the average current in microamperes (if the maximum current is considered, the constant becomes 709) during the life of a drop, n is the number of faradays of electricity required per mole of the species involved in the electrode reaction, D is the diffusion coefficient of the reducible or oxidizable substance in the units of cm^{-2} per second, C is its concentration in millimoles per liter, m is the rate of flow of mercury from the dropping capillary electrode expressed in units of mg per second, and t is the time in seconds for the formation of one drop of mercury.

For reversible reactions involving a reduction process, the relation of the potential and the current at any point on a polarographic wave at 25° is given approximately by the Nernst-type equation,

$$E = E^0 - \frac{0.0591}{n} \log \frac{a_{\text{red}}}{a_{\text{ox}}}$$

where a_{red} and a_{ox} are, respectively, the activities of the reduced and the

oxidized forms of the active species at the electrode interface. However, molar concentrations are usually substituted for activities in polarographic work, since potential measurements are seldom more accurate than a few millivolts.

Substituting the relationship $i = KC_oD^{1/2}$ for the concentrations of oxidized and reduced forms at the electrode interface, the equation becomes

$$E = E^0 - \frac{0.0591}{n} \log \frac{i}{i_d - i} + K'$$

where i is the current at an applied potential E, and i_d is the diffusion current. From the curve in Figure 18.13 it is apparent that the ratio of the concentration of the reduced form to that of the unreduced form at the electrode interface is equal to the ratio $i/(i_d - i)$.

At the half-wave potential one-half of the oxidized species which reaches the electrode is reduced to the corresponding reduced form. Then, at this point, $i = (i_d - i)$, and the equation becomes

$$E_{1/2} = E^0 + K'$$

The constant K' is usually neglected, since it is a very small number involving the logarithm of the ratio of the diffusion coefficients, which ratio is very near unity. E^0 is then replaced by $E_{1/2}$ in polarographic work. If the metal, formed by the reduction process, amalgamates with the mercury, then $E_{1/2}$ equals E^0 minus a potential equivalent to the energy of the amalgamation process.

If the circuit resistance (microelectrode, solution, reference electrode) is appreciable, the applied potential must be corrected for the iR drop through the solution. If a reference electrode other than a saturated calomel one is used, the potential is usually referred back to the calomel electrode.

The qualitative aspect of polarography is based upon the half-wave potential. In most cases the value of the half-wave potential can be shown to be independent of concentration of reducible or oxidizable substance, provided that the composition of the solution is kept constant with respect to foreign salts.

CHAPTER 19

OTHER METHODS OF MEASUREMENT

Chapter 11 lists a considerable number of different kinds of methods of measurement. Of these, only titrimetry, gravimetry, colorimetry, and electrometry have been discussed thus far. The first three methods of this group have long been used, and currently they remain very important. Part of electrometry, potentiometry, is by no means new, and the other part, polarography, is becoming increasingly important.

This selection does not mean that other kinds of methods are unimportant; quite the contrary is true. Some, in fact, are invaluable, especially in certain fields, and for certain kinds of materials. For example, literally millions of determinations are made every winter in the United States of the effective concentration of radiator antifreeze solutions by means of specific gravity measurement. As another example, a popular lecture on emission spectrometry is entitled "Analyses by the Million."

The four kinds of methods emphasized in preceding chapters seem relatively the most important for the purposes of an elementary course in which the aim is to give the student a broad viewpoint on the general principles, means, and methods of making analyses. In contrast, the methods of simple densimetry, just mentioned, are of great practical importance, but they give a student little training to tackle a problem of devising a method of analysis for a complicated polycomponent system.

Furthermore, there is not time in an elementary course to take up all the kinds of methods suggested in Chapter 11. Even if there were, equipping and maintaining a laboratory for large classes with modern instruments becomes very expensive. Yet even in an elementary course students should learn that there is something beyond what is emphasized in this book. Most students who are not chemistry majors have no formal training after the elementary course, and often this course is only one semester in length.

With this viewpoint in mind, the author has included in this chapter brief statements for selected methods other than those already discussed. An inquiring student may thus broaden his perspective and find suggestions for further reading.

The methods selected should be considered only as a sampling of the over-all possibilities.[1] Instruments that may be used range from such simple and inexpensive devices as hydrometers to such intricate and expensive equipment as indicating emission spectrometers and recording mass spectrometers. The treatment here accorded the respective instruments is obviously unbalanced, but any adequate description of the spectrometers is beyond the space available.

The general plan for each method is to state the fundamental principle of the measurement involved, discuss briefly the equipment used, and mention important applications of the methods.

VOLUMIMETRY[2]

As was stated in the discussion of gravimetry, all material things possess mass. In theory, then, any desired constituent, or one chemically equivalent to it, can be weighed if it can be suitably isolated. In a general way the difficulties of weighing increase from solids to liquids to gases.

Volume is likewise a property possessed by all bodies, at least under specified conditions of temperature and pressure. Presumably, in this case, too, one could measure the volume of any constituent, if it were suitably isolated. However, measurement of volumes, especially those of solids, is not as feasible as mass measurements; however, the method is very important in some areas. Volumimetry is considered here in terms of its applicability to solids, liquids, and gases.

In Chapters 12 to 15 the term "titrimetric" was employed to designate methods in which the desired constituent is determined from the amount of a standard solution found to be equivalent to it. The student should keep in mind, when using reference works in analytical chemistry, that the term "volumetric" has been applied very generally to such methods.[3]

[1] The statements included here are necessarily brief and superficial. For a broader perspective of the methods included, as well as various others, see such works as the following: Berl, ed., *Physical Methods in Chemical Analysis,* Academic, 1950-51; Boltz *et al., Selected Topics in Modern Instrumental Analysis,* Prentice-Hall, 1952; Ewing, *Instrumental Methods of Chemical Analysis,* McGraw-Hill, 1954; Gibb, *Optical Methods of Chemical Analysis,* McGraw-Hill, 1942; Weissberger, ed., *Physical Methods of Organic Chemistry,* Interscience, 1945-46; and Willard, Merritt, and Dean, *Instrumental Methods of Analysis,* Van Nostrand, 1951.

[2] Occasionally one finds the spelling "volumetry."

[3] It is inapplicable for titrations made by weighing the titrant, the practice followed in very precise work.

In this book the term "volumetric" is reserved for those methods in which volume is measured as a specific property of the desired constituent.

Principle

The general principle of volumetric methods consists in measuring volumes of solids, liquids, and gases.

The units employed are usually the milliliter or the cubic centimeter, or some multiple or fraction thereof. The National Bureau of Standards has approved the liter and its subdivisions for volume measurements in titrimetry, as discussed in Chapter 4. Presumably this approval extends to measurement of liquids in other kinds of methods.

The physical state of the sample, together with certain other factors, gives rise to several variations in methods of volumetric measurement. The constituent to be measured may be obtained as a gas from solid, liquid, or gaseous samples. Thus, in gas analysis the sample is usually a gas, and the percentage of the constituent is most conveniently expressed on a volume basis. The actual volume of the constituent may be determined either directly or by difference. If the gaseous constituent comes from a solid, as in the determination of nitrogen in many organic compounds by the Dumas method, the mass of the nitrogen is calculated from its volume (at the measured temperature and pressure), and from this value its percentage by weight is obtained.

When the desired constituent is measured as a liquid or a solid, the percentage is likely to be expressed on a weight basis, although with liquid samples the volume basis is often used. The experimental difficulty of relating the volume of solids to their mass may make it expedient to calibrate the measuring vessel empirically in terms of known amounts of the constituent to be determined.

Means of Measurement

The means of measuring the volume of solids, liquids, and gases vary, of course, because of the properties of matter in these different states.

Solids. Measurement of the volume of solids, in the forms such substances assume when separated by the familiar processes, presents a difficult practical problem. No doubt, this difficulty accounts for the small use made of such measurement. For measurement of volume, a given amount of a specific material must assume a definite size. This result is almost impossible to achieve.

Curdy silver chloride AgCl, and hydrous ferric oxide $Fe_2O_3 \cdot xH_2O$, are well-known examples of precipitates having uncertain volume characteristics. The same amounts of magnesium ammonium phosphate hexa-

hydrate $MgNH_4PO_4 \cdot 6\ H_2O$ in two beakers may occupy very different volumes. Obviously, inability to prepare such substances in reproducible particle size renders their volumetric measurement impossible.

In a few instances such measurement is satisfactorily practical. In general, it is limited to cases where only a small amount of a solid can be precipitated in a finely divided, well-crystallized form. Even then, empirical calibration of the container may be necessary.

As an example of such measurement, sodium magnesium triuranyl acetate hexahydrate $NaMg(UO_2)_3(C_2H_3O_2)_9 \cdot 6\ H_2O$ may be used as a precipitating form to separate sodium in water analysis. The precipitate is collected by centrifugation in the bottom of a container with a capillary tube such as that illustrated in Figure 19.1. Calibration of the tube would be made by precipitating and handling known amounts of sodium in the same way as the amount to be used for the unknown sample.

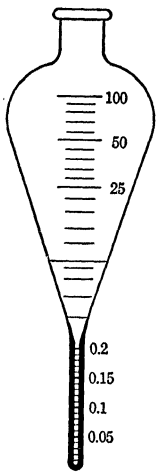


Figure 19.1
Goetz centrifuge tube.

Liquids. Measurement of the volume of liquids of low vapor pressure presents no problem at atmospheric pressure. In fact, there are no significant differences from the operations described in Chapters 4 and 24.

Because of the mechanical conditions under which the liquid is obtained, one finds variations in the form of measuring vessel used. In ordinary distillation separations, for example, such as that used for the data of Figure 7.5, the different "cuts" of the distillate might be collected in simple graduated cylinders. Incidentally, such a procedure could be called a "volatilization-volumetric method," thus indicating that the separation was made by volatilization and the measurement by volumimetry. Some distillation apparatus designed for quantitative separative applications has a roulette-type set of receivers, which make it easy to change for collecting successive fractions.

A somewhat different receiver is illustrated in Figure 19.2. The figure shows a diagram of part of the apparatus recommended for determining water in petroleum products or bituminous materials. The procedure consists in distilling the sample, along with a volatile immiscible solvent, in the round-bottom flask. When the sample mixed with the volatile solvent is heated, the water and much of the solvent distill over into the graduated trap at the lower end of the condenser. The water, being heavier than the solvent, forms a layer at the bottom of the tube, where its volume may be read from the graduations.

Gases. The variables in the statement of Boyle's gas law, $PV = nRT$, should be recalled in connection with the problem of measuring a gas by volumetric means. Disregarding nR in the equation, we have pressure P, volume V, and temperature T, as variables. As every student in freshman chemistry should know, a gram-molecular weight of a gas (e.g., 32 g of oxygen) occupies 22.4 liters at 760 mm and 0°. At different temperatures and pressures the volume will be different. Obviously, then, to apply volumetric measurement to a gas, we must have the temperature and pressure under control.

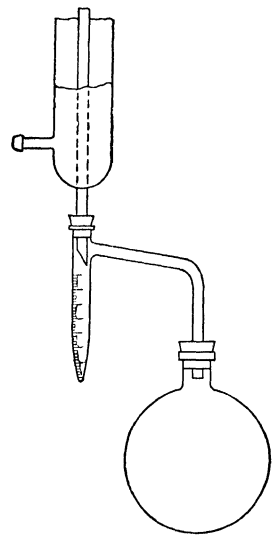


Figure 19.2

Apparatus for volumetric determination of water.

As with measurement of constituents in the liquid state, the problem of volumetric measurement of gases is basically simple. Measuring vessels must be closed, of course, to confine the gas, but they are graduated in milliliters or cubic centimeters, in a manner entirely similar to that of vessels for liquids.

The over-all appearance of most equipment for the measurement of gases appears superficially, at least, very different from that for solids or liquids. Often the major portion of such apparatus consists of parts for evolving and/or separating the desired gaseous constituent from other components of the sample.

In essence, the measuring vessel for gases is usually a gas buret. A simple form is shown schematically as *A* in Figure 19.3. Since the actual readings on the buret are for the confining liquid used in the buret, the technic is quite like that for burets used in titrimetry. The temperature and/or pressure must not change, of course, during a series of readings. In case of change, correction must be made therefor.

The physical state of the sample material is of some interest from the viewpoint of how the desired constituent becomes available for measurement. From solid samples a gaseous constituent is usually liberated by heating and/or chemical action. Carbon dioxide can be evolved from calcium carbonate by heating alone above 800°, or by adding a strong acid and heating the solution near boiling. Steels are heated to fusion

in order to pump out dissolved gases. Carbon in alloy steel is burned out as carbon dioxide by heating the sample at about 1200° in a stream of oxygen.

Liquids present much the same problem as solids except for the use of lower temperatures if they are heated. As an example, urea in urine

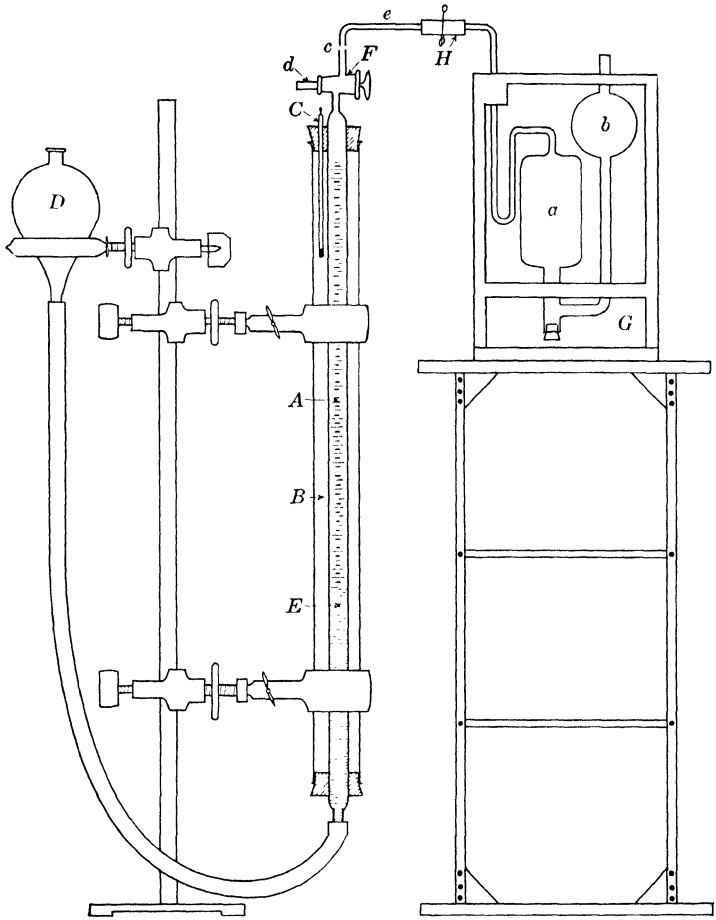


Figure 19.3

Simple gas analysis apparatus. *A*, gas buret; *B*, water jacket; *C*, thermometer; *D*, leveling bulb for adjusting height of confining liquid (mercury or water) *E*; *F*, stopcock; *G*, absorption pipet; *a*, yellow phosphorus chamber; *b*, water chamber; *H*, clamp; *e*, fine-bore capillary tubing; *c* and *d*, outlets.

may be determined by treating the sample with hypobromite to liberate nitrogen, according to the equation

$$CO(NH_2)_2 + 3\ NaOBr \rightarrow N_2\uparrow + CO_2\uparrow + 2\ H_2O + 3\ NaBr$$

The carbon dioxide may be absorbed in a solution of potassium hydroxide, and the volume of the nitrogen then measured.

To obtain one gas from a gaseous mixture usually necessitates resorting to a separation of the type described in Chapter 10. The general technic of this kind of gas analysis may be illustrated by reference to Figure 19.3.

In order to illustrate application of this technic, assume that it is to be used for the determination of oxygen in the laboratory air. To make the determination, open the stopcock to the atmosphere at either of the outlets shown and raise the level bulb until the mercury just enters the stopcock. To draw the sample into the buret, lower the bulb until the meniscus of the confining liquid drops to the bottom of the buret. Fill the buret with a sample and close the stopcock.

To make the determination of the oxygen, adjust the bulb until the meniscus of the liquid in it is at the same height as that inside the buret. Note the reading on the buret and record the volume of the sample taken. The temperature and pressure should not be allowed to change much from here on, unless suitable correction is made therefor.

By means of fine-bore capillary tubing and a piece of heavy-wall rubber tubing, connect the phosphorus Hempel-type pipet (assumed to be charged for use) to the outlet (c), having previously opened the clamp and forced the water in the pipet tube out to the end of the capillary tube. Turn the stopcock, to discharge the gas through the outlet. Raise the level bulb to push the sample over into the absorption pipet, and allow the confining liquid to follow nearly to the bulb of the pipet. Then fasten the level bulb at a height where the meniscus of the confining liquid just comes into the stopcock. After allowing a few minutes for the oxygen to react with the phosphorus, draw the sample remaining back into the buret by lowering the level bulb. Then push the gas back into the pipet and repeat the process several times to allow time for the reaction to go to completion. Finally, draw the residual gas back into the buret until the water in the pipet rises to the level at which it stood before the gas was pushed over into it, and close the stopcock.

Adjust the leveling bulb once more until the menisci inside and outside the buret are at the same height. Read the volume of residual gas. From the decrease in volume, the percentage of oxygen *by volume* may be calculated,

This brief description gives some idea of a common technic for handling gases, as compared to common gravimetric and titrimetric technics.

Figure 19.4 shows a much more elaborate instrumental assembly designed for handling various polycomponent gaseous samples.

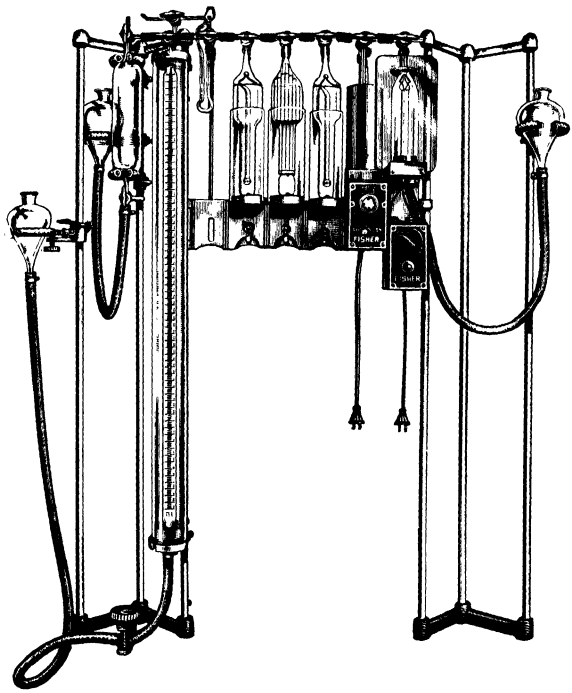


Figure 19.4

Fisher "unitized" apparatus for polycomponent gas analysis (courtesy Fisher Scientific Co.).

Applications

As already indicated, experimental difficulties have made measurement of the volume of solids of little use. Apparently the unsolved problem is to isolate the constituent to be determined in a reproducible physical state.

Such measurement of liquids, however, is relatively common. An excellent, widely used example is the collection of liquid organic compounds following distillation separation. Important also, but less used, is the distillation of water from samples that cannot be heated directly without the evolving of something besides water (see Figure 19.2).

Especially to be noted in this connection is the rapid Babcock method for determining fat in milk. It is widely used in control laboratories where milk is purchased on the basis of its content of butterfat, or where it must meet a minimum specification, as defined by legal statute. The proteins are dissolved by means of sulfuric acid and the fat is then brought to the top of the liquid by centrifugation. The percentage of fat is read off directly when standard test bottles are used. Different forms of bottles are required for milk, skim milk, and cream.[4]

Without a doubt, the outstanding example of the application of volumetric measurement is in polycomponent gas analysis. From the time of the introduction of Hempel's pipets and burets to the present, such methods have been more or less standard. The apparatus illustrated in Figure 19.4 shows recent equipment of this type for the determination of carbon dioxide, oxygen, unsaturated hydrocarbons, hydrogen, carbon monoxide, methane, ethane, and nitrogen (by difference).

Three other typical applications may be cited as examples of these important measurements. The Dumas method for nitrogen in organic compounds has already been mentioned. On burning of the compound under suitable conditions, the nitrogen is evolved as such, and its volume is determined in a gas buret.

A significant development in steel analysis is the increasing application of a volumetric method for carbon. The element is evolved as carbon dioxide, the volume of which is then measured. A great advantage of this method is its rapidity, as compared to gravimetric or titrimetric measurement.

A more homely use of volumetric measurement is in the determination of carbon dioxide in baking powder through measurement of the volume of gas evolved on treatment of the sample with sulfuric acid.[5]

DENSIMETRY

Some of the simplest of all analytical procedures are based upon measurements included under the name *densimetry;* on the other hand, a few densimetric methods are very exacting experimental procedures.

Principle

Before considering the technics of densimetry, it is necessary to recall certain definitions and conventions regarding the usage of terms. Several methods of expressing results are in more or less common use.

[4] Assoc. Offic. Agr. Chemists, *Methods of Analysis,* p. 233 (1950).
[5] *Ibid.,* p. 118.

Density is defined as the mass of unit volume of matter. The principle of densimetry is implied in this definition.

In science, using the metric system of weights and measures, the density of a given substance is the weight in grams of 1 ml of the substance. For solids, cubic centimeters might be used instead of milliliters.

Specific gravity is the ratio of the weight of any volume of a substance to the weight of an equal volume of some other substance taken as a standard. Thus, specific gravity is relative density. The standard is usually water for solids and liquids, and air for gases. With water at 4° as the standard, the density of a substance is also its specific gravity, since, by definition, 1 ml of water weighs 1 g at this temperature. According to this preferred method of expressing specific gravity, the result of a given measurement yielding a value of 1.118 at $t°$ would be stated as specific gravity $t°/4° = 1.118$.

To avoid experimental difficulties of working at 4°, the measurements are commonly made at some more convenient temperature $t°$. The expression sp.gr. $t°/t° = 1.118$ would then show that 1.118 is the ratio of the density of the substance at $t°$ to that of water at the same temperature. Multiplication of this value by the density of water at $t°$ will yield the specific gravity at $t°/4°$. Also multiplication of the value at $t°/t°$ by the ratio of the density of water at $t°$ to that at $t_1°$ will yield the specific gravity at $t°/t_1°$. These statements should indicate the importance of specifying temperature in connection with such measurements.

Unfortunately, the data of densimetric measurements are not always stated in terms of density or specific gravity. Publications abound with values given in a variety of systems, too extensive to review here. A few are mentioned in the discussion on instruments.

Means of Measurement

Densimetric methods are applicable to systems in the gaseous, liquid, and solid states. Since measurements of liquids are used most for analytical purposes, the limited discussion presented here is restricted to this kind of system.

In all cases the application of such methods presupposes the prior construction, from known systems, of curves or tabular data co-ordinating concentration and the property measured. Every chemical handbook contains such tables for a number of common chemicals.

Hydrometers. A hydrometer is essentially a floating device consisting of a bulb, weighted at the bottom, with a slender upper stem, on or

in which is a graduated scale. Sometimes the technic of measurement with hydrometers is known as *hydrometry*.

In use, a hydrometer of suitable range sinks in a liquid until the stem is partly immersed. With a given liquid, having the temperature for which the hydrometer was calibrated, the instrument will sink to a definite depth. This depth depends upon the displacement of the liquid, which in turn depends upon the density of the liquid.

The general form of most hydrometers is illustrated in Figure 19.5A. The type illustrated in Figure 19.5B is similar except that it contains a small thermometer to show the temperature of the liquid tested. All instruments of these two types are used by being placed in the liquid to be tested. Often the liquid itself is placed in a glass cylinder of suitable dimensions. Nearly everyone is familiar with the method used by garage and filling station attendants when they test battery acid or radiator antifreeze solutions by drawing up the liquid into a tube containing the hydrometer.

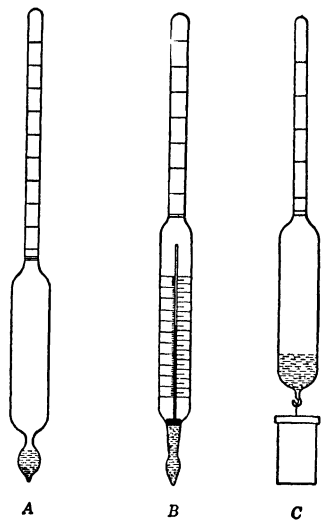


Figure 19.5

Forms of hydrometers.

The Sommer hydrometer, Figure 19.5C, is used for viscous liquids. The sample is placed in the brass cup suspended from the hook at the bottom of the glass bulb and then the hydrometer with cup are placed in a glass cylinder containing water at the proper temperature. A similar arrangement, for use with limited amounts of sample, is found in urine hydrometers. They have a small compartment near the bottom in which the urine sample is placed.

Hydrometers vary most in the scales used in the stem for expressing the results. Probably the most widely used is the specific gravity scale. It seems the logical selection, except perhaps where a different scale indicates directly the amount of some given constituent. Examples of the latter are the New York Board of Health lactometer for water in milk, "saccharometers" for sugar solutions, and "alcoholometers" for alcohol solutions.

For specific gravity measurements of a general nature on samples ranging from light to heavy liquids, a desirable combination consists of

a set of some 20 hydrometers, each covering a different portion of the entire range. Such sets usually include a "finding" spindle, containing a thermometer, for determining which one of the set to use and whether the temperature is that specified for the set. With such a set, the analyst can read, with some uncertainty, to three decimal places.

Most hydrometers are made to be used at a specific, marked temperature in order to have their scales apply. A few are made with a thermometer and supplementary scale that shows, for a specific use, what correction to apply at any temperature other than that for which the main scale was designed.

In addition to the specific gravity scale, several dozen arbitrary scales have been proposed and used to some extent industrially. Occasionally such a scale is widely used. In fact, several are common in connection with the commercial handling of liquids.[6]

Of these arbitrary scales the Baumé system is the most common for general work. This system really consists of two scales, one for liquids heavier than water, such as aqueous solutions, and one for those lighter than water, such as petroleum products. The arbitrary systems selected for establishing the Baumé scale have differed considerably, with the result that confusion may be found in the chemical literature. If one knows the basis for a particular instrument, interconversion of specific gravity and Baumé degrees is possible. One system in use is based upon the following relationships, in which S = specific gravity at 15.56° and B = degrees Baumé:

$$S = \frac{145}{145 - B} \qquad \text{and} \qquad B = 145 - \frac{145}{S}$$

for liquids heavier than water, and

$$S = \frac{140}{130 + B} \qquad \text{and} \qquad B = \frac{140}{S} - 130$$

for liquids lighter than water. The value 145 (and also 140) is known as a modulus. The different systems depend upon different modulus values.

A second system for general measurements is that of Twaddell. Density D and degrees Twaddell Tw are related according to the expression,

$$Tw = 200(D - 1)$$

In the Brix system, the hydrometer "degrees" show the percentage of sucrose in a solution. Density D and degrees Brix Br are related accord-

[6] See Lange, *Handbook of Chemistry*, p. 1106, Handbook Publishers, 1952, for a list of some of the hydrometers and the relation between the different scales.

ing to the expression

$$Br = \frac{D - 1}{0.00388}$$

The interrelationships of several of these scales is shown graphically in Figure 19.6.

Westphal plummet. The Westphal plummet is essentially a small glass cylinder containing a thermometer, for use in determining specific gravity by immersion in a liquid, as shown in Figure 19.7. A measurement involves determining the weight of the liquid displaced by the plummet. Calibration in water gives the displacement of the standard liquid.

Figure 19.7 shows the method of using the plummet on an ordinary Westphal balance provided with rider weights. The beam adjustment should be such as to bring the pointer to a balanced position with the dry plummet suspended from the stirrup.

To measure a substance the plummet is totally immersed, as shown. The proper combination of weights on the beam necessary to bring the pointer to the original zero point gives directly the specific gravity at $t°/t°$. Four decimal places may be read, although the accuracy of the last one is questionable. The largest weight placed at 10 on the beam should just counterpoise the plummet immersed in pure water at the marked temperature. Such balances are also made with a chainomatic device instead of separate weights.

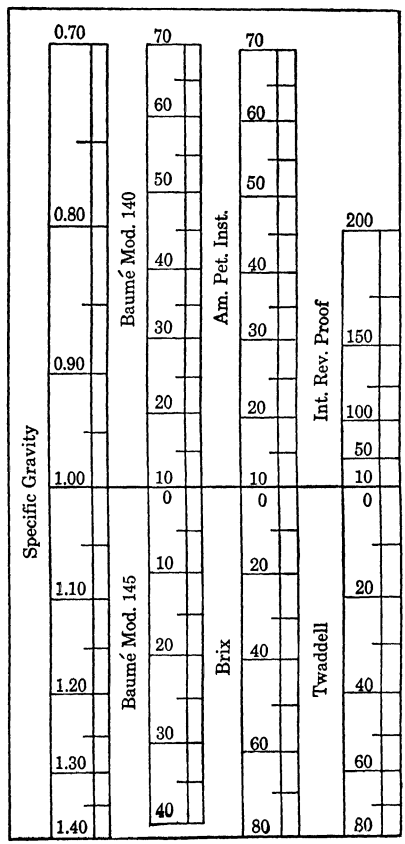


Figure 19.6

Relation of several hydrometer scales.

More accurate results may be obtained by using an analytical balance instead of the Westphal instrument. A small bench, accompanying

many balances, is placed in a position to straddle the left pan and the cylinder containing the test liquid is set on the bench underneath the stirrup hook of the balance. The plummet may then be suspended from the hook and immersed in the liquid at $t°$. The liquid displacement is the difference between the weight necessary to counterpoise the dry plummet in air and that necessary when the plummet is immersed in the test liquid. Dividing this value by the displacement for water at the same temperature gives the specific gravity at $t°/t°$.

Plummets should be calibrated by weighing. Most of them have a displacement at the specified temperature of 5.0000 g. To obtain the displacement, determine the difference in weight of the plummet on an

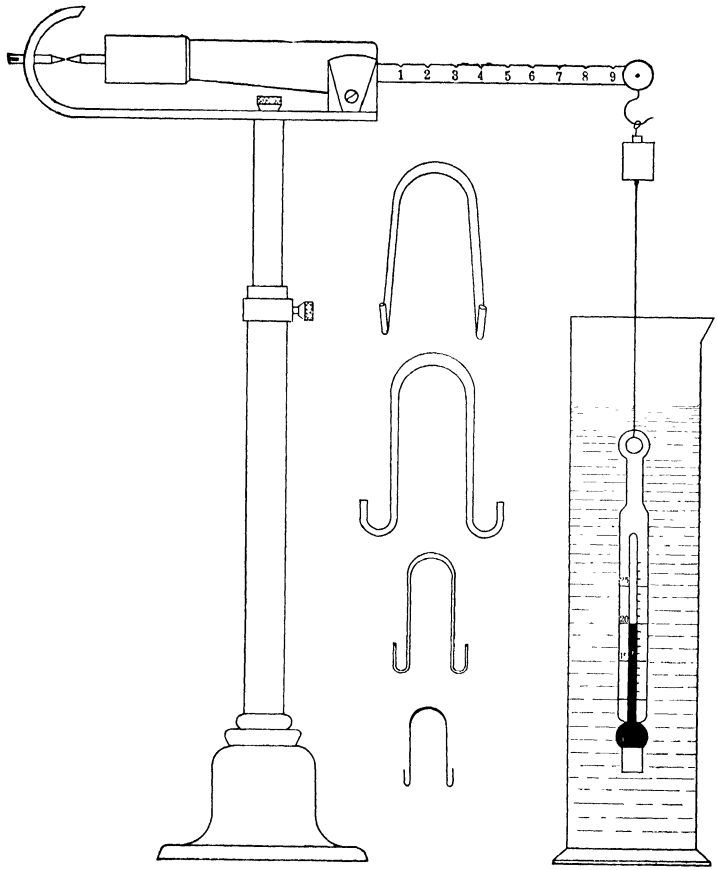


Figure 19.7

Westphal balance.

analytical balance and in pure water at the specified temperature. If the water displacement d is not 5.0000 g, a value obtained experimentally with the plummet should be multiplied by the factor $5.0000/d$ to obtain the true specific gravity at $t°/t°$.

Picnometers. A more accurate method involves the use of a picnometer. This instrument has various forms, but it is essentially a flask or pipet. Picnometers filled with the liquid to be measured are weighed and are weighed again filled with pure water. The ratio of the two masses gives the specific gravity at $t°/t°$.

Common designs of the flask and pipet forms are shown in Figure 19.8. Some flask forms are fitted with a thermometer that is ground into the neck to serve as a stopper. A vacuum jacket on the bottle facilitates work with more volatile liquids.

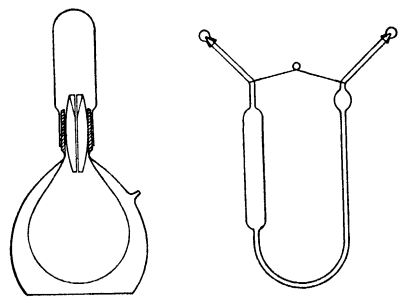


Figure 19.8

Forms of picnometers.

Other methods. Still greater accuracy may be achieved for liquids by the use of a submerged-float method, such as that devised by Lamb and Lee.[7]

Applications

From what has been stated, it is evident that the concentration of many binary liquid systems are susceptible to measurement through a

TABLE 19.1

DENSITY VALUES OF AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID AT 20°/4°

Composition		*Specific Gravity*	*Baumé Degrees*	*Twaddell Degrees*
Per Cent	g/l			
1	10.03	1.0032	0.5	0.64
2	20.16	1.0082	1.2	1.64
4	40.72	1.0181	2.6	3.62
6	61.67	1.0279	3.9	5.58
8	83.01	1.0376	5.3	7.52
10	104.7	1.0474	6.6	9.48
20	219.6	1.0980	12.9	19.60
30	344.8	1.1492	18.8	29.84
40	479.2	1.1980	24.0	39.60

[7] Lamb and Lee, *J. Am. Chem. Soc.* **35**, 1666 (1913).

determination of their specific gravity or density. However, if accuracy in the calculation of concentration is to be satisfactory, there must be sufficient variation of the specific gravity with concentration.

The data of Table 19.1 for hydrochloric acid are of interest. For aqueous solutions of several concentrations there is given for each solution the corresponding reading in terms of specific gravity, degrees Baumé, and degrees Twaddell.

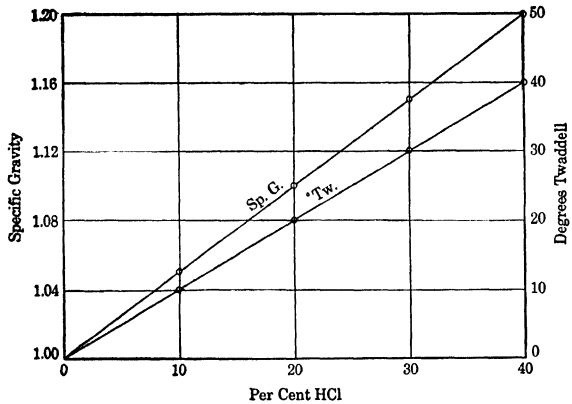


Figure 19.9

Curves co-ordinating concentration of hydrochloric acid and the values for specific gravity and Twaddell readings.

Figure 19.9 shows graphically the relationship between concentration of hydrochloric acid and two of the other values, specific gravity and degrees Twaddell.

An important point here is the change in the instrument reading corresponding to a given change in concentration. The table and the figure together indicate something of the refinement of measurement that would be required to achieve a determination accurate to 0.1 per cent of the quantity measured. Although such refinement of technic is possible, usually it is too exacting experimentally to be justified.

Actually, such methods are used widely and extensively. Every chemical handbook contains many pages of such data for common liquids and solutions of common acids, bases, and salts. Perhaps the most familiar example is to be seen at gasoline filling stations where the attendant checks the acid in the storage battery and the antifreeze solution in the automobile radiator.

The determination of ethanol in alcoholic liquors is another fine ex-

ample. In this case the analyst must distill out the ethanol (along with some water, of course), make the distillate up to a definite volume, and then determine the specific gravity by means of a picnometer. Reference to standard tables,[8] if the official method has been followed, enables one to read off the percentage of ethanol. In this particular case, the percentage may be desired by weight or by volume.

REFRACTOMETRY

Light has different speeds in transparent media of different densities. In general, the speeds bear a rough inverse proportionality to the densities.

Principle

As a beam of light passes from a medium of one density into another medium of different density, there is not only a change of speed but also of direction, unless the incident beam is normal (perpendicular) to the interface of the two media.

The general effect is illustrated in Figure 19.10 in which A is the medium of less density and B that of greater density. The angle of incidence between the normal to the interface and the incident beam is represented by i, and the angle of refraction between the normal and the refracted beam is represented by r. The index of refraction n, of medium B relative to medium A is defined as $\sin i/\sin r$. The numerical value is greater than unity when the density of medium B is greater than that of medium A.

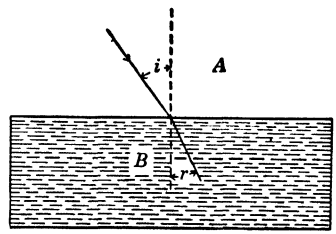


Figure 19.10

Refraction of light beam. A, medium of less density; B, medium of greater density; i, angle of incidence; r, angle of refraction.

In the design of refractometers an important point concerns the effect of having the angle of incidence only slightly less than 90°. To illustrate what happens, consider a thin film of liquid to be measured spread on the surface PR of the prism PQR in Figure 19.11. If the monochromatic light beam AB has an incident angle of exactly 90°, it is said to be at the critical angle of incidence. If one considers the beam as passing in the direction CBA, and if the angle c is somewhat greater than shown, the portion BA would not pass beyond the surface of the prism.

[8] Assoc. Office Agr. Chemists, *op. cit.*, p. 836.

Now consider the direction ABC. On being refracted through the prism along the path BC, c measures the angle of refraction. CD marks the path after the beam leaves the prism and travels to the ocular O. A second beam, $A'BC'D'$, has a different path and reaches the ocular on the bright side of the visual field. As the position of the prism is changed, there is a change in the relative proportions of the light and dark parts of the visual field.

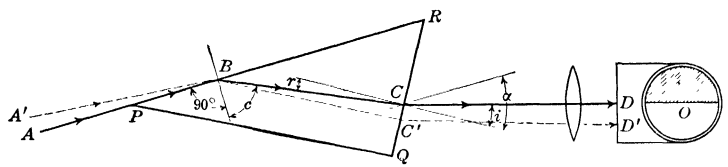


Figure 19.11

Light path at critical angle of incidence. PQR, prism; $ABCD$, path of light beam at critical angle of incidence; c, angle of refraction; O, ocular.

It may be shown that

$$n_s = \cos \alpha \sqrt{n_p^2 - \sin^2 i} + \sin \alpha \sin i$$

where n_s = the refractive index of the liquid under test on the prism face PR, n_p = the refractive index of the prism, α = the angle between a line normal to RQ and one parallel to PR, and i = the angle between the normal to RQ and the emergent beam CD. Different values of the angle α will be found in such refractometers as the Abbé, dipping, and butyro instruments, which are designed for measuring different substances.

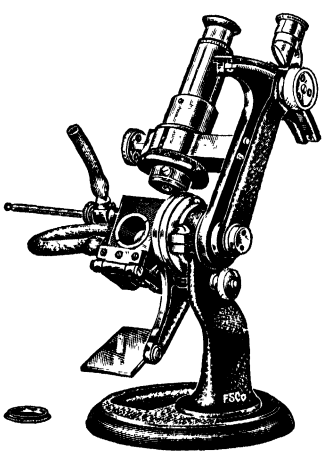


Figure 19.12

Abbé refractometer.

Since light of different wavelengths is refracted to different degrees, and since different media have different refractive capacities, conditions must be specified. Unless otherwise stated, refractive index is generally understood to refer to the use of the D line of sodium and to light passing from air into the medium being considered.

Means of Measurement

The two most common instruments for measuring refractive index are the Abbé type, and the Zeiss immersion type of refractometers.[9] A brief description of the principles of their construction follows:

Abbé refractometer. One form of the Abbé type of instrument is illustrated in Figure 19.12. Figure 19.13 shows the arrangement of the essential optical parts. Light from the point sources of the ground-glass surface passes through the liquid specimen and meets the main prism

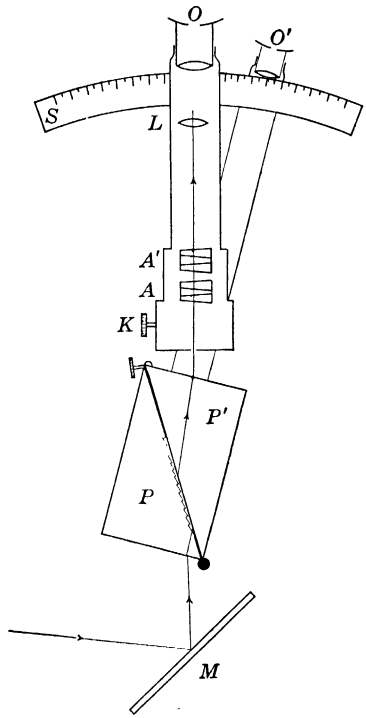


Figure 19.13

Light path in Abbé refractometer. M, mirror for reflecting light into the instrument. Prism P is mounted on a hinge so that it will swing back to permit placing a few drops of the test liquid on the face (the jagged line represents a ground surface for diffusing the light). On closing of the prism by the bolt at the top, a film of liquid separates prism P from prism P'. A and A', Amici compensating prisms, coaxial with the telescope, which can be rotated simultaneously in opposite directions by means of knob K; L, converging lens; O, ocular for observing the position of the line dividing the dark and light portions of the visual field; O', ocular for observing the value of the refractive index on the graduated sector S.

(PQR in Figure 19.11) surface at grazing incidence, where it is refracted at the critical angle into and through the telescope. If the source is monochromatic, the visual field will be sharply separated into a bright and a dark portion.

Since daylight or electric light sources are more convenient, Abbé instruments have long been equipped for them. These heterochromatic

[9] See "Bausch and Lomb Refractometers," Catalog D-202, 1950, Bausch and Lomb Optical Co., for descriptions of one manufacturer's late models.

sources make the division line in the visual field colored and nebulous on account of the different degrees of refraction of the different wavelengths constituting the white light. Two Amici prisms are included to compensate for this dispersion.

Figure 19.14 represents the effect of a single Amici prism on a beam of white light. It will be noted that the yellow *D* beam of the polychromatic light passes through with its final direction unchanged. All other wavelengths are refracted. This effect is achieved through a proper selection of dispersive power and facial angles for the component prism parts. Two such prisms, which can be rotated in opposite directions to suitable positions, are sufficient to compensate the dispersive effect of the liquid-prism system and thus eliminate the zone of spectral hues at the dividing line in the visual field. Since the direction of the *D* line of sodium, which is used for the calibration, is not changed, the reading for the refractive index is unaffected.[10]

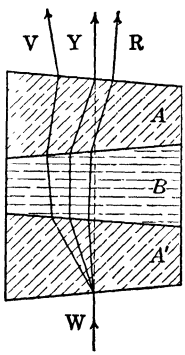


Figure 19.14

Amici prism. W, white light; R, red wavelength; Y, yellow; V, violet. In the composite prism *A* and *A'* are crown glass and *B* is flint glass.

The compensator scale, used in conjunction with tables accompanying the instrument, provides a means for measuring the mean dispersion of the sample.

The Abbé instrument is convenient and rapid to use. Temperature control may be achieved by circulating water through the jackets surrounding the prisms. Only a few drops of liquid are needed for measurement. The film between the prisms is so thin that some color or turbidity does not interfere. The scale usually is made to read refractive index directly from 1.3008 to 1.7108, with a precision of about two units in the fourth decimal place. Some scales are graduated in terms of the percentage of some given constituent.

Immersion refractometer. Figure 19.15 shows the working assembly and Figure 19.16 illustrates the general arrangement of the optical parts of the immersion, or dipping, type of refractometer.

The usual instrument has a range from 1.325 to 1.366. Five other interchangeable prisms, covering the range from 1.365 to 1.544, are available. The internal scale itself is graduated to read from −5 to +105. Table 19.2, provided with the instrument, serves for determining the re-

[10] The new Bausch and Lomb high-precision instrument uses a sodium-arc illuminant, with no compensator. Its precision of reading is said to be approximately ±0.00003 (see instruction booklet).

fractive index corresponding to a given scale reading with the first prism.

A precision of 3 or 4 units in the fifth decimal place may be attained if the scale reading is within 0.1 division.

Volatile liquids may be placed in a special metal cup that fits over the end of the instrument. An auxiliary prism, in conjunction with this cup, provides for the use of a few drops of liquid.

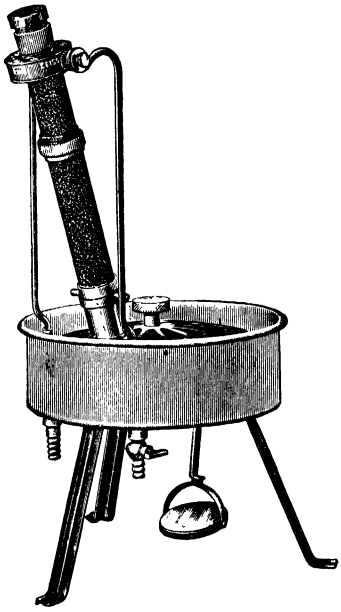


Figure 19.15

Immersion refractometer assembly.

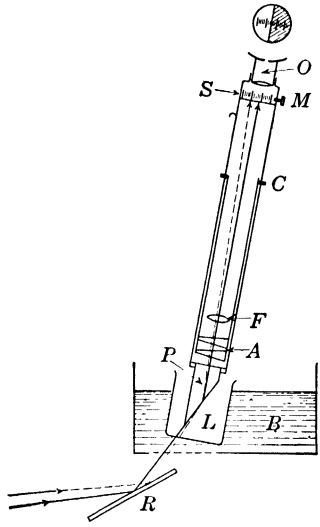


Figure 19.16

Light path in immersion refractometer. *R*, mirror for reflecting light through the bottom of the temperature control bath *B* into the beaker containing the test liquid *L*; prism *P*, Amici prism *A*, and converging lens *F* function as in the Abbé instrument; *C*, collar for rotating the Amici prism; *S*, scale on which the light is focused; *M*, micrometer screw for moving the scale; *O*, ocular.

Other refractometers. For general or special purposes a number of other refractometers have been designed.[11] Among these may be mentioned Amagat and Jeans' oleo-refractometer, Fery's refractometer, Dawes' refractometer, and the Zeiss butyro- and sugar refractometers. The Pulfrich type is of special value when the refractive index and disper-

[11] See Reilly and Rae, *Physicio-Chemical Methods*, II, 334, Van Nostrand, 1953.

sion are desired for specified spectral lines. The light source is monochromatic.[12]

Perhaps the most accurate of all such instruments is the interferometer. It is applicable, in different forms, to liquids or gases. The refractive

TABLE 19.2

SCALE READING-REFRACTIVE INDEX VALUES

Scale	*n*	*Scale*	*n*	*Scale*	*n*	*Scale*	*n*
−5	1.32539	23	1.33625	51	1.34687	79	1.35714
4	78	24	67	52	724	80	50
3	618	25	705	53	61	81	86
2	57	26	43	54	98	82	822
1	96	27	81	55	836	83	58
0	1.32736	28	820	56	73	84	94
+1	75	29	58	57	910	85	930
2	814	30	1.33896	58	47	86	66
3	54	31	934	59	84	87	6002
4	93	32	72	60	1.35021	88	38
5	932	33	4010	61	58	89	74
6	71	34	48	62	95	90	1.36109
7	3010	35	86	63	132	91	45
8	49	36	124	64	69	92	81
9	87	37	62	65	205	93	217
10	1.33126	38	99	66	42	94	52
11	65	39	237	67	79	95	87
12	204	40	1.34275	68	316	96	323
13	42	41	313	69	52	97	59
14	81	42	50	70	1.35388	98	94
15	320	43	88	71	425	99	429
16	58	44	426	72	61	100	1.36464
17	97	45	63	73	97	101	6500
18	435	46	500	74	533	102	35
19	74	47	37	75	69	103	70
20	1.33513	48	75	76	606	104	605
21	51	49	612	77	42	105	40
22	90	50	1.34650	78	78		

index can be determined close to one unit in the seventh decimal place. This is equivalent to about two parts per million for a solution of sodium nitrate. In air, 0.01 per cent of carbon dioxide is detectable by this means. Interferometers are not widely used.

Applications

Refractometry includes the methods in which refractive index is of interest both as an indication of the purity of a substance and as a means

[12] For instructions for the operation of the Pulfrich refractometer, see Findlay, *Practical Physical Chemistry*, Longmans, 1923.

of determining the concentration of a substance. The latter application is of greater interest to the quantitative analyst.

Examples of the use of Abbé refractometers as a means of control include edible, essential and other oils; fats and waxes; sugar, syrups, glue, and gelatine; petroleum products; and varnish.

Two examples of official methods employing the refractometer may be cited. One is the determination of solid matter in sugar solutions with the Abbé instrument,[13] and the second is the determination of methanol in distilled liquors with the immersion instrument.[14]

POLARIMETRY

One of the older optical methods of measurement has long been known as polarimetry.[15] Although definitely limited in applications, because of the specific nature of the property measured, this method does have an important place.[16]

Principle

The transverse wave motion in a beam of ordinary light occurs in all possible planes that include the axis of propagation. Certain transparent media, in transmitting such a beam, suppress these vibrations in all but one plane, thereby producing "plane-polarized" light.

The plane of polarization of such a beam is rotated to the right or left on passage through certain substances. Consequently, such substances are said to be optically active. For a given active substance both the direction of rotation and the magnitude of the angle are specific properties. The quantitative application of the phenomenon rests upon the relation of the angle of rotation to the concentration of a solution of the active substance.

Dextro-rotatory substances rotate the plane of polarization to the right, and laevo-rotatory substances rotate it to the left. The former are indicated by the sign (+) and the latter by (−).

The specific rotation, or specific rotatory power, of a substance, serves as a basis for characterization. It may be defined as the angle of rotation produced by a column of solution 10 cm long and containing 1 g of active substance per ml.

[13] Assoc. Offic. Agr. Chemists, *op. cit.*, p. 495.

[14] *Ibid.*, p. 132.

[15] Since the property of rotatory power of a substance is measured, the name might more consistently be "optical rotatimetry."

[16] See Brown and Zerban, *Physical and Chemical Methods of Sugar Analysis*, Wiley, 1941, and also Bates *et al.*, "Polarimetry, Saccharimetry, and the Sugars," *Nat. Bur. Standards*, Circ. 440, 1942.

Since the angle of rotation is a function of the wavelength of the illuminant, monochromatic light is used in general polarimeters. Usually the source is sodium light. The symbol $\overset{20}{}_{D}$ is used to express the specific rotation at 20° for the *D* line of sodium light.

In general, the specific rotation of an active substance in solution may be represented by the expression

$$[\alpha]_D^{20^\circ} = \frac{100\,\alpha}{bc}$$

where α = the angle of rotation for a column b dm long and containing c g per 100 ml. Table 19.3 gives representative values for a few substances.

TABLE 19.3

SPECIFIC ROTATIONS

Substance	$[\alpha]_D^{20^\circ}$
Camphor (in benzene)	+41.4
Lemon oil	+63.0 (±4)
Nicotine (in benzene)	−164.0
Orange oil	+97
Sugars	
Dextrose	+53.1
Invert	−20.6
Lactose	+52.5
Levulose	−93.3
Maltose	+137.5
Sucrose	+66.5

Means of Measurement

For the most general type of measurement, the analyst needs (1) a source of monochromatic light, such as sodium light; and (2) an instru-

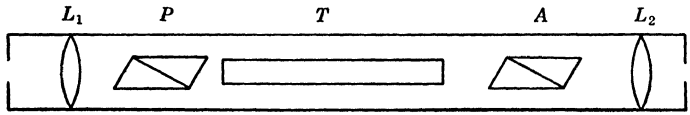


Figure 19.17

Schematic diagram of parts of a polarimeter. L_1, lens to collimate the entering monochromatic light beam; *P*, fixed Nicol prism (the "polarizer") to polarize the light in a definite plane; *T*, tube of definite length to hold the liquid or solution; *A*, second Nicol prism (the "analyzer"), which can be rotated about the axis of propagation of the polarized beam; L_2, lens system for observation of the rotation. Not shown is a circular scale to show the angle prism *A* is rotated.

ment, generally known as a polarimeter. The essential parts of the polarimeter are shown schematically in Figure 19.17.

To exemplify the use of such an instrument, consider that a definite weight of cane sugar syrup is diluted to a definite volume, and that one then determines the angle of rotation[17] for a column b dm long. The concentration c of the sugar is calculated in g/100 ml from the expression

$$c = \frac{100\ \alpha}{66.5\ b}$$

in which α is the observed rotation, b is the length, and 66.5 is the specific rotation for sucrose.

A modified instrument, known as a saccharimeter, is adapted particularly for determining sugars. Reference works should be consulted for details of construction, including the use of direct-reading scales, such as the Ventzke, the Laurent, and the International.

Applications

Probably the most extensive use of such methods is in the determination of various sugars in sugar-containing products. As with a number of other physical properties, such as refractive index, specific rotation of a substance is often determined to assist in characterizing the material.

Obviously, this method is applicable only to systems that can rotate plane-polarized light. Practically, such compounds are not encountered in large numbers in industrial analysis. Those most likely to be found are organic compounds having an asymmetric arrangement of different elements or groups around at least one carbon atom in the compound.

TURBIDIMETRY AND NEPHELOMETRY

In the course of their formation from a solution the particles of a precipitate inevitably reach a size characteristic of colloidal dispersions. This phenomenon was mentioned in the discussion in Chapter 8. When the particles reach suitable size, the system becomes turbid or opalescent on illumination with a light beam, because of scattering of the light.

Principle

The general principle involved may be considered with reference to Figure 19.18. Any decrease in intensity of I_0 produced by the suspended particles will arise as a result of absorption and/or scattering of the light. The measurement problem involves relating the magnitude of these effects to the amount of the desired constituent dispersed.

[17] The operator does not polarize the sample, as stated in some publications.

Quantitative measurement of a constituent in such a dispersed state rests primarily upon one's success in the following operations: (1) preparation of the dispersed phase (usually a solid) in reproducible particle size, including maintenance in this state long enough for measurement; and (2) measurement of the absorbing or scattering effect of the particles upon a light beam incident upon them.

Preparation of the disperse system is often difficult, both as to obtaining desired particle size and keeping the particles that way.[18] Usually, the analyst maintains the opposite of the conditions recommended for producing a filterable precipitate. Thus, colloidally dispersed silver chloride is readily obtained with very dilute solutions of hydrochloric acid and silver nitrate by pouring the solutions together quickly at room temperature with a minimum of mixing. In addition, a stabilizer or protective colloid may be used to aid in holding the substance in the desired range of particle size long enough for measurement.

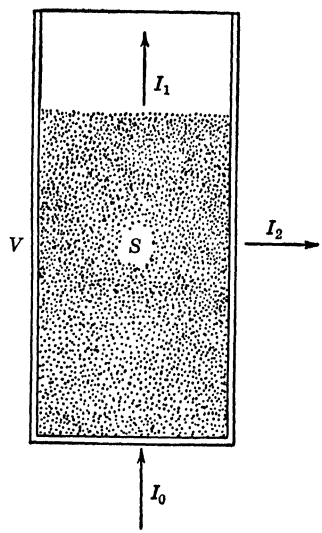


Figure 19.18

Diagram of a light beam incident upon a disperse system. V, glass cell; S, solid particles dispersed in liquid medium; I_0, incident light beam; I_1, part of I_0 transmitted; I_2, part of I_0 reflected by particles in the system.

Means of Measurement

Two kinds of instruments have been developed, the difference between the two depending principally upon whether the transmitted or the reflected light is to be measured. In general, *turbidimeters* measure transmitted light, and *nephelometers* measure reflected light.

The over-all arrangements of accessory parts in a turbidimeter are analogous to those for a filter photometer such as that illustrated in Figure 17.8 (page 263). Similarly, a photoelectric nephelometer has essentially the arrangement of the fluorescimeter illustrated in Figure 19.19 (page 324). Some filter photometers are equipped with accessories for all of these measurements.

[18] See Yoe, *Photometric Chemical Analysis*, Vol. II, Wiley, 1929, for a summary of early work.

Applications

The dispersion of a solid in a liquid has been the chief kind of system measured by this method. The extensive use of precipitates would seem to indicate the possibility of many turbidimetric or nephelometric measurements; however, two reasons account for their limited use. In the first place, only very small amounts of any precipitate can be maintained in a satisfactory dispersed state. In the second place, control of the process of producing suitable particle size is difficult in most cases, and this variability leads to low precision in the measurement.

At the moment, the tide of popularity for this kind of measurement seems to be at an ebb, a state somewhat attributable, no doubt, to the advent of a variety of other instruments for measuring other properties of substances.

The method is relatively rapid, and extensive use has been made in some cases. Thus, the Parr sulfur photometer was developed for the routine turbidimetric determination of sulfur in coal. The precipitate of barium sulfate is formed from the residue left in the bomb following a determination of the B.t.u. value of the coal. Similarly, thousands of turbidimetric determinations of sulfate in water have been quickly made.

A recent application is to monitor the turbidity of systems in process, such as feed water in high-pressure boilers. On process streams the operation has been automatized to the extent of indicating or recording turbidities. In one direction, it becomes a matter of measuring clarity of water, oils, solvents, and solutions.

FLUORESCIMETRY

Many substances, either as such or after reaction with some reagent, fluoresce on irradiation with ultraviolet radiant energy. The occurrence of fluorescence, and often its characteristic appearance, serve for various qualitative purposes. If the intensity of the light emitted is a function of the amount of a desired constituent, a quantitative method may also be feasible.

Principle

Fluorescimetry is closely related in principle to colorimetry. In colorimetric methods the radiant energy reaching the eye (or photocell) is part of that incident upon the sample. In fluorescimetric methods, however, the radiant energy reaching the detector is different in wavelength from that of the exciting incident beam. The source provides invisible ultra

violet rays and the fluorescing medium emits rays in the visible region of the spectrum.

Means of Measurement

The schematic diagram of Figure 19.19 illustrates the essential parts of a simple two-cell fluorescimeter.[19] Generally, the photocells are the photovoltaic type.

Although there is considerable similarity between this instrument and the filter photometer described in Chapter 17, several important differences may be noted: (1) the source (e.g., a mercury-arc lamp) must emit

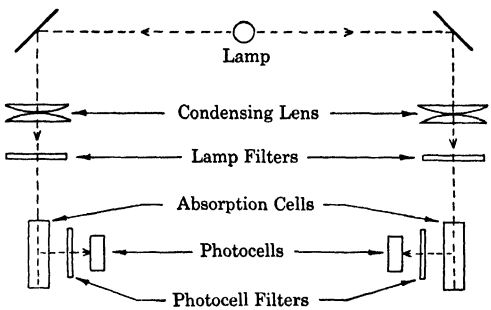


Figure 19.19

Schematic diagram of simple two-cell fluorescimeter.

ultraviolet radiant energy, filters generally being necessary to restrict the wavelengths passed to particular spectral lines or narrow bands; (2) only visible radiant energy is passed by the photocell filters; and (3) the beam of radiant energy incident on the photocell leaves the absorption cell in a direction at right angles to that of the beam entering the absorption cell.

Some spectrophotometers have accessories for easy conversion of the instrument for measurement of fluorescence.

Applications

One of the outstanding current applications of fluorescence measurements is in the determination of uranium, following fusion with sodium fluoride.[20] The variety of both inorganic and organic applications is evident in the reviews of White.[21]

[19] The names "fluorimeter" and "fluorometer," sometimes used, might be taken to mean an instrument for determining fluoride.

[20] See Rodden *et al.*, *Analytical Chemistry of the Manhattan Project*, p. 537, McGraw-Hill, 1950.

[21] White, *Anal. Chem.* **21**, 104 (1949); **22**, 69 (1950); **24**, 85 (1952); **26**, 129 (1954); see also, Radley and Grant, *Fluorescence Analysis in Ultraviolet Light*, Van Nostrand, 1954.

MANOMETRY

In the analysis of gases, one must deal with three variable quantities: volume, pressure, and temperature. A previous section described the possibility of measurement of the volume of a constituent in the gaseous state by working at a known (or fixed) pressure and temperature. Such a determination is based upon the measurement of a change in volume resulting from the absorption of a constituent from the sample.

As an alternative procedure, one may fix the volume and the temperature and then measure the change in pressure resulting from the absorption of some constituent from the gaseous mixture, or the pressure developed by a single constituent isolated for measurement. Such procedures are known as *manometric.*

Principle

In manometric methods, the gas to be measured is confined in an accurately defined volume, at constant temperature, and under pressure from a column of mercury. Then the height of the mercury column is measured. Readings to the nearest millimeter may suffice, but if more precise values are desired, a cathetometer or measuring microscope is required. In the more precise measurement, correction should then be made for the capillary depression of the mercury in the manometer tube.

There are two variations in the general principle of manometric measurement. In one, the pressure measurement is merely incidental to the calculation of the weight of the gaseous constituent measured. In the other, the pressure measurement alone suffices.

In the first variation, the analyst measures the pressure of a gaseous constituent isolated for measurement. Both the volume and the temperature of the gas should be noted. Since the kind of gas is known, and since a gram-molecular weight of the gas occupies 22.4 liters at 0° and 760 mm mercury pressure, the weight of the given gas, the pressure of which is measured, can then be calculated. In general, the number of moles of a gas n, at a pressure P mm, a temperature T°K., and contained in a volume of V ml is given by the gas law equation

$$n = PV/62{,}360\ T$$

In Chapin's method for the determination of carbon dioxide in carbonates,[22] the volume of the gas at standard conditions is calculated and multiplied by the weight of 1 ml of carbon dioxide at standard conditions ($44/22{,}400 = 0.001965$). Specifically the relationship is

[22] *J. Ind. Eng. Chem.* **10**, 527 (1918).

$$\text{Weight of } CO_2 = \frac{V \times P \times 273 \times 0.001965}{760 \times (273 + T)}$$

In the second type of manometry, one measures pressure only. We may refer again to a previously cited example, that is, that 32 g of oxygen occupy 22.4 liters at 0° and 760 mm mercury pressure. If the amount were reduced to 24 g and the volume and temperature remained constant, the pressure would then be correspondingly reduced to 570 mm ($^{24}/_{32}$ of 760). In practical measurements, on a gaseous mixture, the desired constituent is removed by suitable means, such as absorption, adsorption, or other action. Then the percentage reduction in pressure is the percentage of the constituent removed, or

$$\% = 100 \times \frac{P_1 - P_2}{P_1}$$

where P_1 is the initial pressure and P_2 is the pressure after removal of the constituent.

It will be noted that the volume and the temperature need not be known, as long as they do not change during the measurement.

Means of Measurement

Since manometric methods have not achieved wide use among analysts for general work, manometric apparatus is not common except in biochemistry.

The apparatus suggested by Chapin[22] for determining carbon dioxide in carbonates shows the use of simple equipment for the incidental application of manometry to obtain the weight of a desired constituent.

For such incidental use, however, the finest example of a manometer is that designed by Van Slyke and Neill.[23] An external view of one model of this apparatus is shown at the left in Figure 19.20. The gas bulb, shown in cross section at the right in Figure 19.20, is graduated for volumes of 0.20, 2.00, and 50.00 ml.

Although many of the applications of this apparatus are for incidental readings of pressure in order to calculate weights later, P_1 and P_2 readings may be obtained and used, as suggested already. To obtain these values, the gas liberated from a sample is such that it can be removed by a suitable reagent, after which a second pressure reading is taken. An example is carbon dioxide, which can be removed by absorption in sodium hydroxide solution.

In many of the applications a sample, such as blood, is introduced by appropriate means into the bulb, and a suitable reagent is introduced

[23] *J. Biol. Chem.* 61, 523 (1924); see also Peters and Van Slyke, *Quantitative Clinical Chemistry*, II, 267-442, Williams and Wilkins, 1932

through the graduated tube. The ensuing reaction, accompanied by shaking, if necessary, liberates the gas to be measured. After adjusting the mercury column to bring the gas to one of the three designated volumes, the pressure is read in *E*. The water jacket provides for measurement of the temperature.

Pitts, DeFord, and Rektenwald [24] designed a modified apparatus which requires only 2 to 6 ml of gas sample and employs "bead" reagents for

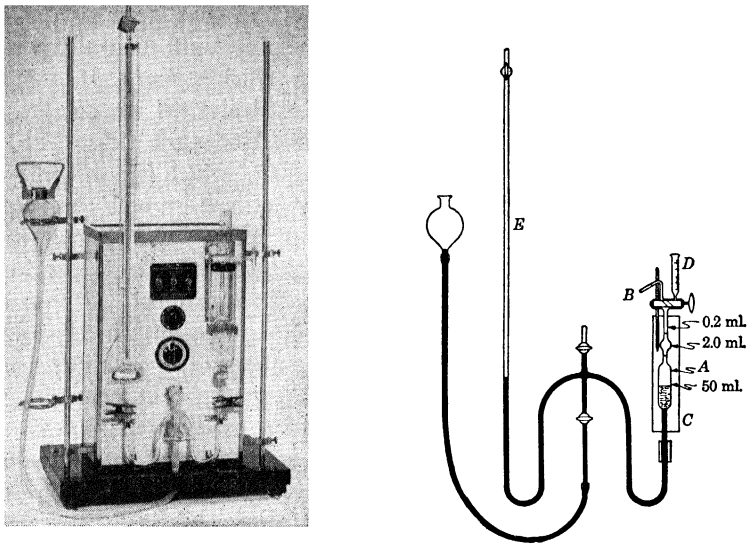


Figure 19.20

Van Slyke and Neill manometer (photo, left, courtesy Arthur H. Thomas Co.). At right: *A*, bulb; *B*, exit tube; *C*, water jacket; *D*, graduated tube; *E*, manometer tube.

selective removal of the components in the sample. The essential features of this unit, shown in Figure 19.21, are a reaction cup immersed in a beaker of mercury so that reagent holders can be introduced under mercury into the chamber, a water-jacketed gas pipet of approximately 5 ml volume, and a spherical expansion chamber, about 3.5 cm in diameter. The volumes are not critical. The confining volume of the pipet is indicated by two fiducial marks, M_1 and M_2, inscribed on the capillary tubing as indicated. The pipet is connected to the manometer tube by a ball-and-socket joint. The upper end of the manometer tube terminates in a stopcock.

A side arm, *SA*, extends to the back of the apparatus and is connected

[24] *Anal. Chem*, **24**, 1566 (1952).

to a 50-ml hypodermic syringe. The syringe plunger is guided by a screw-driven bar. The syringe is filled with mercury and the rotation of the feed screw makes possible the forcing of mercury from the syringe into the pipet and manometer.

To operate the apparatus, a gas sample is introduced through the side arm, or directly into the reaction chamber. The amount of sample is measured by withdrawing the syringe plunger and thus drawing the sample into the pipet until the trailing mercury column reaches mark M_1. Stopcock S is closed and the gas compressed or expanded to mark M_2. The initial pressure P_1, which is a measure of the amount of the sample, is noted. A reaction, such as the removal of moisture from the sample, is performed in the reaction chamber. Stopcock S is opened and the gas forced back into the chamber. The desired reagent (in this case phosphorus pentoxide in the form of a bead on the end of a bent wire) is introduced into the reaction chamber. After the reaction is complete, the gas is drawn back into the pipet until it is contained between the marks M_1 and M_2. The pressure P_2 is again measured. The substance removed from the gas sample was present to the extent of $100(P_1 - P_2/P_1)$ per cent. A side arm serves for connecting the syringe unit to the manometric unit.

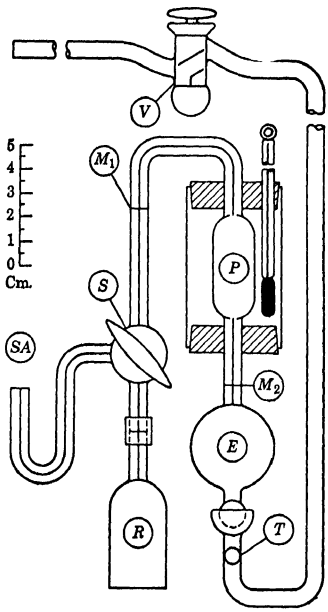


Figure 19.21

Schematic diagram of pipet and manometer units. R, reaction cup; P, gas pipet; E, expansion chamber; S and V, stopcocks; T and SA, side arms.

Applications

Since manometric methods are based upon measurement of pressure, they apply only to systems in the gaseous state. For this purpose, however, they have distinct merit, especially for very small quantities of the order of a cubic millimeter. Even when the gas is expanded to a comparatively large volume, its pressure may be readily measured.

The most extensive application of manometry has been in biochemistry,

where the Van Slyke and Neill apparatus is well known. There is no inherent limitation of the technic to this area.

Peters and Van Slyke recommend this apparatus particularly for determining blood gases. In addition, they include many detailed directions for determining organic nitrogen and carbon, amino nitrogen, urea, sugar, lactic acid, iodates, calcium, sulfates, potassium, nitrates, and others.

An interesting, if less elegant, method has been suggested for the manometric determination of carbon dioxide in beer by observing a direct reading on a gauge.[25] A piercing apparatus punctures the top of the container and permits escape of the gas to the pressure gauge.

EMISSIMETRY [26]

The methods discussed in Chapters 17 and 29 are based upon the *absorption* of radiant energy by desired constituents. Consideration is limited therein to procedures involving color, that is, the visible region of the spectrum. The region of the spectrum in which the maximum absorption occurs is often referred to as an *absorption band.*

Another very important technic involves the *emission* of radiant energy by desired constituents. Emission methods of measurement are the subject of this section.

Principle

Every chemist knows that sodium chloride, for example, when heated hot enough in a gas flame, imparts the familiar yellow hue to the flame. He knows also that the more sodium there is, the more intense, within limits, is the color. Heating the salt volatilizes the elements and raises the outer-shell electrons to higher energy levels. As these electrons return to their normal orbits, energy is emitted, especially of wavelength 589 mμ for the sodium. This wavelength gives rise to the sensation of yellow in the normal human observer.

This phenomenon serves as a delicate qualitative test for sodium. When operating conditions are suitably controlled, the intensity[27] (amount) of the color serves as a quantitative measure of the sodium.

If the light from the sodium flame is allowed to act on a photographic

[25] Bray and Stone, *Anal. Chem.* **10,** 15 (1938).

[26] The nomenclature for these methods is inconsistent and confusing. The word "emissimetry" is used here as co-ordinate with "absorptimetry," the term employed in Chapter 17. Other terms often found are the adjectives "spectrographic" and "spectrochemical," and the nouns "spectrography" and "spectrochemistry." The nouns "emission spectrometry" (or "spectroscopy") and "flame photometry" appear less frequently.

[27] *Intensity* $\times$ *time* may be considered as the radiant flux.

plate or film in a suitable instrument (see Figure 19.25, page 334), an image of the slit appears as a narrow line on the developed plate for each different wavelength of radiant energy emitted. The instrument must have enough dispersive capacity to separate the lines. These separate images are referred to as the *spectral lines* of the element. Such lines are illustrated for cadmium and zinc, in Figure 19.22. Some elements show many lines and some a much smaller number. For a given element, some lines are much more intense than others.

Often the line selected for use in measurement is in the ultraviolet, rather than the visible, region of the spectrum. Most likely it is one of the strongest of the lines emitted, but interference by lines of other elements present may make some less intense lines preferable in a given case.

The photographic plate, or a print made therefrom, is often referred to as a *spectrogram*. The spectrogram shown in Figure 19.22 illustrates further the principles of emissimetry.[28]

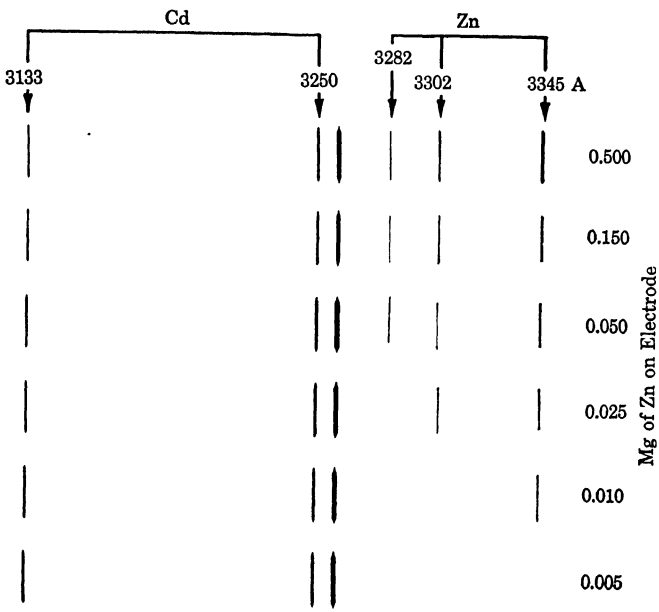


Figure 19.22

Spectra of cadmium sulfate and zinc.

[28] The author is indebted to Professor Thomas De Vries for the spectra of Figures 19.22 and 19.24.

These spectra were obtained by vaporizing samples in an arc and registering the radiant energy emitted by means of a photographic plate after the various wavelengths of radiant energy had been dispersed by the grating of a spectrograph. The darkest spectrum lines for zinc were produced by 0.50 mg of zinc in a 50-mg sample of cadmium sulfate. The other spectra, in descending order, were obtained from samples containing 0.15, 0.05, 0.025, 0.010, and 0.005 mg of zinc. The three lines for zinc, at 3282, 3302, and 3345 A, increase in sensitivity, in this order. None of these zinc lines is visible when 0.005 mg is present. The lines for cadmium all have the same degree of blackness, as the exposure times were the same.

A widely used method for employing such spectra for quantitative determinations made photographically is to construct a working curve

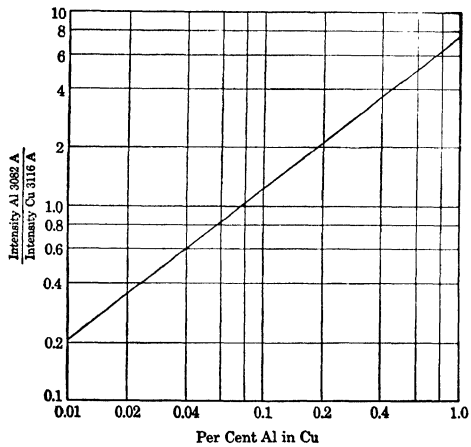


Figure 19.23
Working curve.

co-ordinating blackness (optical density) of lines with concentration of desired constituent. Because of variability of emulsions on plates and films, together with differences in development technics, a correlation is usually first obtained in the form of an emulsion calibration curve. This curve relates the intensity of the radiant energy emitted to the degree of blackness it produces in the emulsion.

In addition, because of variability in the rate of vaporization, together with fluctuations in the arc, it is desirable to compare the intensity of the spectrum line of the desired constituent with the intensity of a line of an internal standard element the concentration of which is constant in any given series of samples. It is generally possible to select such a pair of spectrum lines close together. A working curve for aluminum, with cop-

per as the internal standard, is shown in Figure 19.23. A straight line is generally obtained when the logarithm of the intensity of the spectral line is plotted against the logarithm of the concentrations.

Each of the chemical elements susceptible to spectroscopic detection and identification is characterized by a unique emission spectrum. No two elements have the same number of lines at the same wavelengths. Some lines at particular wavelengths may coincide or overlap, of course. To identify an unknown, one obtains its spectrum and then compares enough of the lines, particularly certain groups of lines, with the lines of known spectra until a match is found. Rather than comparing actual spectra of the unknown with known spectra, the analyst may measure carefully the wavelengths of certain lines and then check these values with tables of the wavelengths of all the usable spectra. The "MIT Tables" are famous for this purpose.[29]

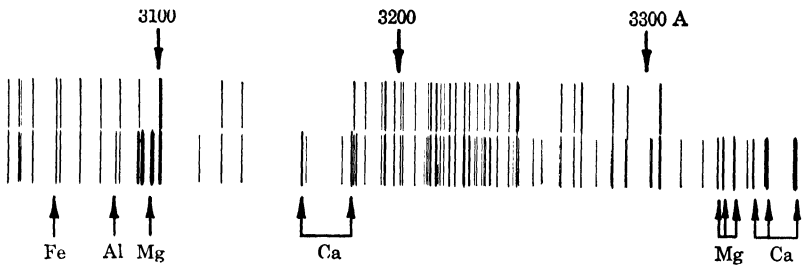


Figure 19.24

Spectra for iron (top) and a sample of cement (bottom).

For purposes of qualitative analysis, it is frequently desirable to photograph the iron spectrum, with its wealth of lines, adjacent to the spectrum of the unknown. This aids in the location of lines of the unknown when numerous elements are to be identified in the sample. Such a pair of spectra are shown in Figure 19.24, about one-fifth of the spectrum plate being included here for the sake of clarity of presentation. With the aid of the iron lines in the upper spectrum, the spectral lines for aluminum, calcium, iron, and magnesium can be readily located in the spectrum of cement. It will be noted that many of the lines in the two spectra are identical.

[29] Harrison, *et al., Wave-Length Tables,* Wiley, 1939. See also Lange, *Handbook of Chemistry,* pp. 898-921, Handbook Publishers, 1952; and Hodgman *et al., Handbook of Chemistry and Physics,* pp. 2469-2625, Chemical Rubber, 1953.

Means of Measurement[30]

Although there are many different details in instruments, arranged in a variety of ways, three parts comprise the fundamental units of an emissimeter.

Source. The source, by which the sample is volatilized, provides the radiant energy to be measured. High-voltage arc and spark sources are widely employed. The high temperatures reached are necessary for volatilizing many of the metals. In a flame photometer, used for more easily volatilized metals such as sodium, a fine spray of a solution of the desired constituent(s) is blown into the flame. Many difficulties have been encountered in all such operating technics in the effort to achieve adequate control of the emission process.

Dispersing means. Isolation of the spectral line(s) to be measured is usually accomplished through dispersion of the radiant energy emitted by means of prisms or gratings in the intruments. Many variations in design of instruments have been used.

It may be noted that gratings, in contrast to prisms, give linear dispersion of the spectral lines. Prismatic dispersion may not provide adequate separation of close lines in the red end of the spectrum.

Detector. Measurement of the energy of the spectral line(s) selected is accomplished by using photographic or photoelectric means as detectors. In photographic instruments a film or plate registers the line(s), the intensity (blackness) of the line(s) being proportional to the amount of the constituent(s). In photoelectric instruments a photocell serves. Its response to the energy incident upon it is evidenced in some sort of meter indication.

Figure 19.25 illustrates the fundamental parts of an emission spectrometer. The schematic diagram shows the arrangement for a Littrow type of mounting of a prism. The radiant energy emitted during volatilization of the desired constituent(s) at the arc source is dispersed by the refracting prism, and the spectral lines so separated are photographed on the plate. With instruments of high dispersion, rotation of the refracting prism on a vertical axis brings different parts of the spectrum into the range of the plate.

The Beckman flame photometer consists of an attachment for atomizing a solution into a flame, so mounted that the radiant energy emitted

[30] See such monographs as the following—Brode, *Chemical Spectroscopy,* Wiley, 1943; Harrison, Lord, and Loofbourow, *Practical Spectroscopy,* Prentice-Hall, 1948; Nachtrieb, *Principles and Practice of Spectrochemical Analysis,* McGraw-Hill, 1950; Sawyer, *Experimental Spectroscopy,* Prentice-Hall, 1951.

may pass into the Beckman spectrophotometer (Model DU or B). The Model DU is described in Chapter 17. The proper wavelength setting of the prism permits the desired spectral line to pass, and the response of the photocell is measured on the meter.

One of the heights of analytical gadgetry is reached in instruments of the Quantometer type. In them a dozen or so photocells are mounted so that each one becomes the detector for the radiant energy emitted by

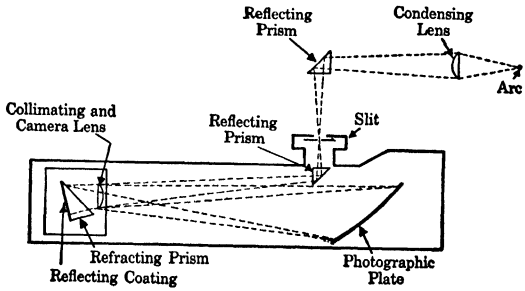


Figure 19.25

Schematic diagram of the optics of a Littrow type of spectrograph.

some selected line for a different element. In one type, attached meters then indicate directly the percentages of the elements for which the photocells were set. These indicators have to be calibrated, of course, in terms of known amounts of the desired constituents handled in the same way as that to be used for the unknown.

Applications

In considering the place of this technic one has to bear in mind that an atomic property is involved. This means, of course, that only elements are susceptible to such measurement. Ions, groups, or compounds cannot be determined in this way.

The elements listed in the upper right-hand corner of the Periodic Table, that is, the nonmetals, are not easily, if at all, determinable with an emissimeter. Perhaps 70 to 75 of the metals are determinable, but not all equally well. It is well known that only a minute amount of sodium is needed to give a sodium flame. This indicates high sensitivity. As such sensitivity is characteristic of the method, the technic is primarily for trace amounts of constituents. Thus, it may be excellent for a substance containing 0.005 per cent of copper, but it cannot be applied, for example, to determine this metal in a copper-base alloy containing 95 per cent copper.

Much of the time the uncertainty in a determination is 1 to 5 per cent of the amount of the constituent determined. Thus, the method does not approach the 0.1 per cent cited as the reasonable goal of good titrimetric and gravimetric determinations.

Any good equipment of this type is expensive, and the partially automatic instruments are very expensive.

Notwithstanding the limitations cited, the applications of such technics in industry and research in the past decade have been phenomenal. As an example, 80 to 90 per cent of the hundreds of thousands of determinations done annually in one metallurgical concern are obtained in this way. Scientific meetings, societies, and journals have devoted themselves to this specialty. In the case of the self-indicating instruments, we find some of our most rapid industrial measurements.

For qualitative detection of the metals in minute amounts, the spectrograph is probably our most valuable analytical tool. The cost of good equipment and the need for training to apply the technic have prevented widespread use in colleges and small industrial laboratories.

RADIOACTIMETRY [31]

Interpretation of the properties of radium led to the conclusion that the element disintegrates spontaneously. This disintegrative process came to be known as *radioactivity,* and the entities produced as *radioactive decay products.* Soon several other elements, notably uranium and thorium, were shown to be radioactive, and potassium was found to be weakly radioactive.

Later work revealed that most elements consist of two or more isotopes, and for elements heavier than bismuth all of these isotopes are radioactive as they occur in nature. A few elements in the middle of the Periodic Table are naturally radioactive. In potassium, already mentioned, the active isotope is one of mass 40, which constitutes only 0.011 per cent of the total element. However, it is possible to base a determination of potassium upon the measurement of this isotope.

Finally came the discovery of the possibility of making elements radioactive by nuclear action produced through bombardment of stable isotopes with different particles. Examples are protons and deuterons from a cyclotron, or, more recently, neutrons produced in a nuclear reactor or atomic pile.

[31] Nomenclature in this area is unsettled. "Radiometry" has been used, but in physics this word may imply measurement of the amount of radiant energy emitted by sources in the ultraviolet, visible, or infrared region of the spectrum.

Principle [32]

Analytical application of radioactivity rests upon the fact that a decaying isotopic species gives off certain products, and that the process of decay occurs at a definite rate. The methods of detection of these products are such that extremely small amounts of the radioactive species can be detected. Hence the method has great sensitivity.

Beside the daughter products formed by the radioactive disintegration process, there are three kinds of "rays" emitted: (1) alpha rays, which are doubly-charged helium ions; (2) beta rays, which consist of electrons; and (3) gamma rays, which consist of electromagnetic waves of very short wavelength, much like X-rays.

Certain properties of these emitted rays are widely used for measurement. Primarily the properties concerned are the ability to penetrate matter and the ability to ionize the matter through which the rays pass. Alpha rays, for example, have a short range of from 1 to 10 cm in air, and can be stopped by a thin sheet of paper. They do have a high ionizing capacity per unit distance traveled. Beta rays, or electrons, are much more penetrating, but they produce less ionization. They differ widely in their energies, the range being from about 0.1 to several million electron volts. Those in the range of 1 m.e.v., for example, can penetrate about 300 cm of air or 1.5 mm of aluminum foil. Gamma rays are highly penetrating, but produce little ionization.

One of the remarkable characteristics of such a disintegrating system is the constancy of the rate at which the rays are emitted. This rate determines the half-life of an isotope. It is defined as the length of time required for the disintegration of one-half of the mass of an isotope. Thus, one-fourth of the isotope would be left at the end of two half-life periods, one-eighth at the end of three half-life periods, and so on to the end. These half-lives are characteristic of the isotope. They range from fractions of a second to millions of years.

The symbol λ is used to designate the rate of disintegration, or fraction disintegrating per unit of time. The exponential equation

$$N = N_0 \times e^{-\lambda t}$$

gives the number of atoms N, left after time t has elapsed, starting with N_0 atoms. Thus, the half-life period is equal to

$$\ln 2/\lambda = 2.303 \log 2/\lambda = 0.693/\lambda$$

[32] For general information see the following: Bleuler and Goldsmith, *Experimental Nucleonics*, Reinhard, 1952; Friedlander and Kennedy, *Introduction to Radiochemistry*, Wiley, 1949; and Rossi and Staub, *Ionization Chambers and Counters*, McGraw-Hill, 1949.

Radioactimetric measurements consist in determining the number of disintegrations per unit of time. Counts per second or per minute is a common terminology. There is a direct correspondence between half-life periods and counts per second. Iodine-131 is a radioactive isotope much used in biological work. It has a half-life of 8.04 days (6.90×10^5 sec.), and therefore a disintegration rate of 1.004×10^6 per sec. For 1 gram-atomic weight of iodine (126.9 g) this means that $6.03 \times 10^{23} \times 10^{-6}$, or 6×10^{17} atoms are disintegrating per second. This calculation emphasizes the extreme sensitivity of this method of measurement, when one realizes that individual disintegrations can be detected and measured.

A unit much used in radioactimetry is the millicurie. It is defined as the amount of radioactive isotope with an activity of 3.7×10^7 disintegrations per second. Thus, only 6.2×10^{-8} gram-atoms (0.008 mg) of iodine-131 represents one millicurie of activity.

Means of Measurement

As a result of the emission of one or more of the entities, helium ions, electrons, or gamma rays, a substance undergoing radioactive decay ionizes the surrounding gaseous medium. The following factors affect the extent of this ionization: (1) the amount of radioactive substance; (2) the nature of the surrounding medium; and (3) the nature and energy of the ionizing particle(s), that is, the kind of nucleus disintegrating.

The problem of measurement is complicated here, particularly if all three products come from two or more different radioactive substances. Screens of different thickness of metals, such as aluminum and/or lead, provide for recognition of different kinds of products emitted.

In early days electroscopes were used for measuring the degree of ionization produced. More recently Geiger-Müller counters have been used extensively. The latter instrument consists of a glass tube lined with a metal cylinder as a cathode and a center wire anode insulated from the outer cylinder. The tube contains a gas or mixture of gases at low pressure. A potential of at least 600 volts is applied across the electrodes. The ionization of the gas in the tube by a high-speed particle, such as a beta ray, produces an electrical impulse which can be counted by a scaling circuit. It takes about 10^{-4} to 10^{-3} seconds for the positive ions of the gas to drift to the wall before a following impulse can be counted. Thus, many counts per second can be observed. At the other extreme, a single count at infrequent intervals may be made.

In a scintillation counter, particularly efficient for detecting gamma rays, a flash of light is produced in a crystal of anthracene or other spe-

cially prepared compound. These light flashes are observed and counted with an electronic circuit in which special photosensitive tubes, usually multiplying phototubes, are employed.

The instrumental part of this field is still quite unsettled, as indicated by the monthly journal, *Nucleonics*.

Applications

Both qualitative and quantitative uses of radioactimetry are of interest. Qualitatively, the analyst is concerned with identifying the isotope(s) present in a sample. This involves measurement of half-life periods, together with identification of the nature of the products emitted by the radioactive species and measurement of the energies of the rays. The change with time of the number of radioactive disintegrations counted with a scaler leads to a knowledge of the half-life period. Tests with different metal foils of known thickness lead to a knowledge of the energies and nature of the rays.

Quantitatively, he is concerned with measuring the number of counts. This value is then compared with the number of counts from a known weight of the isotope under investigation. In such determinations corrections may have to be made for self-absorption of rays by the sample or by the walls of the Geiger-Müller tube used.

Almost daily, laboratories are being newly equipped for making such determinations. Much of the work being done involves the use of radioactive isotopes as a means of studying a wide variety of problems in many different fields.

PART TWO

Laboratory Exercises with Analytical Technics

CHAPTER 20

MANAGING LABORATORY WORK

The achievement of satisfactory results in the analytical laboratory depends upon various factors. Adequate equipment in apparatus, chemicals, and service facilities is assumed. Just as important to the student is the possession of clear and accurate directions for the laboratory work. However, every experienced instructor knows that these things alone will not insure good analytical results. In any large class some students do well and some do not. The purpose of the present chapter is to present certain recommendations for planning and executing analytical work.

The greatest single factor contributing to good work is the innate intellectual capacity of the student. Next in importance is the degree of application exhibited toward the job at hand. Brains alone will not produce analytical data. A genuine interest in the work, accompanied by the will to do, are very important stimulants toward achievement.

USE OF THE TEXTBOOK

The textbook is intended to provide an elementary discussion of the principles underlying quantitative separations and measurements, together with adequate laboratory directions for performing a selected list of typical determinations. These requirements indicate that a book should be studied from the standpoint of its immediate practical value in furnishing information on how to perform certain analytical procedures, and also from the standpoint of its provision of a long-range point of view as to the general nature and application of analytical methods.

The first of these functions of the textbook concerns its use for individual analytical procedures. The assignments for a course consist of a selected number of determinations, many of which involve the use of individual samples. In considering any given procedure, such as the calibration of a buret, the preparation of a standard solution, or the determi-

nation of calcium in limestone by the precipitation-gravimetric method, the student should read carefully the complete directions and note both the various facts upon which the method is based and the general procedure recommended. Any points of chemistry or technic that are not clear to him should be discussed with the instructor.

With such points cleared up, the actual experimental work should be started. It is best to work step-by-step. The procedures should be reread to determine what constitutes the first step and how it is to be done. Suppose it is the measurement of the sample. The particular details should be noted, such as any special method of weighing, the amount of sample to take, whether counterpoised glasses are suitable, and what disposition is to be made of the weighed portion. Then the operation of measurement should be performed as directed. Each of the succeeding steps should be considered and carried through in the same manner.

The second problem of effective use of the textbook concerns its presentation of an over-all view of analytical methods in general. From the hundreds of methods used in industry, the instructor selects a small number which experience has indicated can be studied in the time at the disposal of the average student. The principal basis of selection is the illustration of the application of some general principles.

The precipitation-gravimetric method for determining iron may be taken as an example. The use of ammonium hydroxide as a precipitant and the ignition of the insoluble hydrous oxide to ferric oxide may be considered as typical of the procedure used in determinations of other elements forming such a precipitate. In this case, as in most others, the student should be alert to any special procedures made necessary by the chemical properties of the element to be determined. In this kind of procedure the analyst is always concerned with such details as the following: the solvent, the *p*H of the solution, the best precipitant, the temperature for digestion, the filtering medium, the washing medium, the temperature for igniting the precipitate, and the reaction of the residue to the atmospheric environment.

PLANNING THE WORK

Like many other activities, laboratory work is performed most successfully when it follows a carefully formulated plan. Many students, struggling to complete some determination in an afternoon, seem amazed to learn that it is not uncommon for an experienced industrial analyst to complete 100 of the same determinations per day. What is the difference between such an individual and the beginning student who does well to prepare a solution of hydrochloric acid of an exact concentration in one

laboratory period? To a large extent the skilled analyst's productivity may be attributed to his having acquired, through many repetitions, the necessary technic. This facility, or skill in the art, is discussed briefly in the next section. Probably even more important is the preparation of, and adherence to, a definite plan for executing the work. Large numbers of determinations cannot be done speedily in a haphazard fashion.

In attempting to increase efficiency through planning of the work, the student should direct his attention first to the manner of working. Students who are neat and methodical are likely to be most efficient, and vice versa. It is always a pleasure to the instructor to have a student who is orderly and neat in performing his work and submitting the analytical record of it. Such an individual has a sense of pride in keeping his working space, apparatus, and record book in presentable condition.

It is very important that the student learn early to keep a number of determinations progressing at the same time. Duplicate (or triplicate) determinations on a given sample are generally carried on simultaneously. Where separations of a number of constituents from the same sample are necessary, the student may have to await certain parts of a separation before proceeding with the next constituent. Very often, therefore, he will find it distinctly advantageous to be working on two or three different kinds of samples at the same time. The instructor will always have suggestions for fitting together the different phases of the work.

In preparing a program for making effective use of the laboratory period, the student should study the book at home. The procedures for the samples to be analyzed should be scrutinized carefully and a list made of the successive operations to be encountered. This list should be carefully examined to determine where a "break" occurs, that is where it will be necessary to wait for some operation to be completed, such as the cooling of a crucible before weighing or the digesting of a precipitate before filtration. If no such "breaks" occur, a single sample (in duplicate) may be analyzed straight through at once. If a number of such samples are to be analyzed, the analyst usually handles simultaneously as many as he can, that is, he weighs all of them while he is at the balance and then proceeds similarly with the succeeding steps. When a "break" is reached in a procedure, the wise student will know just what is to be done in another determination and will get it under way rather than loitering around the laboratory until the operation he is waiting for is completed.

In the preparation of such a list of operations to be done in spare moments, it is often of advantage to schedule certain operations for overnight or for time between laboratory periods. Thus, certain precipitates must be digested at room temperature for 12 to 24 hours, and some elec-

trolytic separations may be accomplished very conveniently by being allowed to proceed overnight.

The most efficient use of his laboratory time depends on the student's doing outside it as much preparation as possible. He may just as easily do at home such items as drawing calibration curves for burets, calculating factors, and filling in his notebook in the routine form required for the records.

LABORATORY TECHNIC

The major objectives of the laboratory work in quantitative analysis are to secure analytical data necessary for the determination undertaken and to obtain, insofar as possible, an understanding of the general application of the principles underlying the method used.

In administering a course, the instructor may emphasize either the quality or the quantity of determinations made. There is no question that quantity production is essential in industry as it is presently organized. However, experience with a considerable number of students who had spent some time in industrial laboratories before taking the college course has convinced the author that emphasis should be placed first on securing reliable results. A smaller number of dependable analyses seems preferable to a larger number of analyses of questionable reliability. The superiority of the speedy worker, in general industrial practice, cannot, of course, be denied. Some individuals are naturally more rapid in their motions than others; some are awkward and clumsy in acquiring hand skills, such as handling laboratory apparatus.

While the student should strive first to secure data as reliable as possible, he must not forget that even college laboratories have a given schedule of work to be completed. In the author's course, grades for individual determinations are given on the basis of the degree of agreement of the instructor's and the student's values. Performance of determinations beyond the minimum specified serves both to raise the student's total grade and to extend his analytical experience. Thus, even in college, it is of practical importance to him to do as much creditable work as possible.

In attempting to accelerate his laboratory production, the student should give attention first to careful planning of his program of work, as directed in the previous section. Next in order of attention is acquisition of the approved technic for performing the various necessary operations. There are acceptable forms for executing such work just as there are in pole-vaulting or tennis. In this respect, the instructor's example should be the student's guide. The student should learn not only to use the

correct motions but also to avoid useless motions. Finally, the student must give his attention to the formulation and pursuit of the definite objective of getting more work accomplished. All of these procedures may be summed up as the development of efficiency.

Several recommendations may be made concerning the attainment of this last objective. At the beginning of the laboratory period the student should begin work promptly and energetically. A second recommendation is that he may profitably practice certain operations in blank. Thus, he should learn to control the outflow of a buret so that the meniscus may be stopped at some predetermined point before he begins to calibrate the instrument by weighing. The third recommendation is that the student put forth a definite effort to acquire more rapid motions. Although the practice of some musicians in doubling and quadrupling their original speed of playing scales may not be altogether applicable as an example here, definite attention toward speeding up such individual operations as weighing will yield very worth-while results. Always, of course, approved practices should be developed.

Elimination of carelessness is a very important factor in the development of a technic of maximum effectiveness. In laboratory operations carelessness may occur at many points, recording weights, reading burets, or neglecting to control properly conditions influencing chemical reactions. A student burdened with this characteristic may be expected to submit his record book in the approved form only when he is compelled to do so by some system of penalties. One of the most frequent results of carelessness is the submission of data that are not calculated correctly. Such results are wrong just as truly as if some mistake had been made somewhere in the procedure.

Still another factor in the attaining of speed in analyses amounts really to the application of common sense. Numerous situations arise in which the student may conserve time and energy by giving thought to the requirements of the work in hand. Three examples will illustrate the point. (1) If a solution is to be evaporated on the hot plate, it should be evident to a student with chemical sense that the cover glass should be raised enough to permit vapor to escape readily. (2) The percentage of calcium in limestone cannot exceed that in pure calcium carbonate, that is, approximately 40 per cent. A student should know, therefore, that a report of 50 to 60 per cent is immediate evidence of a large error. (3) Experimental work should be performed with due regard to the required reliability of the data to be secured. With a good analytical balance one can weigh to 0.1 mg. In ordinary good analytical work one can hardly expect to reduce the total error much below one part per

thousand, or 0.1 per cent. Although most weighing is done to four decimal places, this care may be chiefly a waste of time. A 5-g sample of steel weighed to within one point in the third decimal place would involve an error of one part in 5000. In calibrating a 50-ml buret, the water delivered for a 10-ml interval need be weighed no closer than 5 points in the third decimal place since the buret cannot be read closer than 0.01 ml. This factor of measurement is of importance in another way. If directions call for the use of "about" 0.4 g of sample, probably any amount between 0.3 and 0.5 g can be used, but it should be weighed to four decimal places. Specification of "about" 0.4 g of some reagent *to be added in the course of a determination* does not necessitate weighing beyond the first decimal place unless the final results are dependent in some way upon the amount used, as would happen if an impurity for which a correction had to be applied were present, in which case the exact amount of reagent must be known.

CHAPTER 21

MISCELLANEOUS LABORATORY HINTS

Chapter 20 consists of rather general suggestions for the management of laboratory work in quantitative chemical analysis. In a way, these ideas represent "fatherly advice" to the student to give thought to the planning and executing of his analytical determinations.

In addition to such general suggestions, a number of more specific factors in the accomplishment of successful analyses concern the student in a number of ways. These factors involve laboratory work, too, but they relate to particular subjects or operations. Because of their nature, it seems appropriate to describe them briefly at this point. As a whole, they are not particularly related to any specific method of separation or measurement, nor to any individual class of materials being analyzed.

EQUIPMENT

Certain equipment, such as a mercury cathode vessel, serves only one purpose. A number of items, however, are of general utility, and will be discussed here.

Towels

For various purposes in laboratory work the student needs a clean towel. If a vessel is to be weighed after it has been wiped with a towel, the cloth should not leave a deposit of lint or fibrous material on the surface wiped. New toweling really needs washing before it is used to remove such lint (and sizing, if present). An old, often-laundered bed sheet makes a good wiping cloth. It may be made "chemically clean," at least in part, by digestion in dilute hydrochloric acid, rinsing in water, digestion in dilute ammonia, and thorough re-rinsing in water. Distilled water may be the final rinsing medium.

Stirring Rods

As indicated by the name, stirring rods serve for stirring of solutions, as in a beaker during a precipitation reaction. Also, they facilitate transferring of a solution from a beaker to another container, and are used occasionally for other operations.

For 250-, 400-, and 600-ml ordinary beakers, rods 3 to 4 mm in diameter serve. They should be 6 to 8 cm longer than the depth of the beaker in which they are to be used. The ends should be fire polished. In stirring a solution in a beaker the rod should not hit the side of the vessel.

The analyst's "policeman" consists of such a rod over one end of which is slipped a tightly-fitting piece of rubber tubing which is closed (sealed) at one end. Such a rod is useful for loosening a precipitate that sticks in a beaker.

Watch Glasses

For elementary analytical work three kinds of watch, or cover, glasses may be used. The most common is the type used to cover vessels, such as beakers and casseroles. The glass prevents extraneous material from falling into the container, or material inside from spattering out during heating or evaporation.

These glasses are used with the convex side down. They rest on the rim of the container for processes such as dissolution of a sample or digestion of a precipitate. If a liquid in a container is to be evaporated, the glass should be raised a few millimeters above the rim of the vessel by some means, such as glass hooks hung over the rim of the vessel (see Figure 21.1). In a special form of cover, three radial ribs pressed into the glass serve to raise it. On removing a cover glass, one should wash back into the container any condensed liquid or solid material deposited on the under side of the glass.

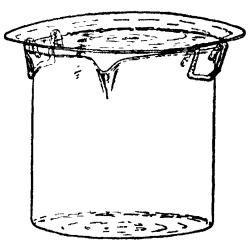


Figure 21.1

Glass hooks on beaker to support watch glass.

Pairs of watch glasses, about 7 cm in diameter and matched (or nearly so) for mass, are often used in weighing. Some analysts call them tared glasses. In use, one glass is placed on each balance pan. The most common application is in weighing solid samples. For this particular purpose some balances have a special glass pan with a small handle to facilitate transferring the weighed sample to a container. Some analysts use these glasses in weighing such objects as crucibles, to avoid possible attack of the pan by corrosive material.

Glasses split in half are useful for covering beakers during the course of electrodepositions, when the electrodes dip into the solution.

Watch-Glass Supports

Double hooks, made of 3-mm diameter glass rod, are useful for raising glasses above the rim of a vessel during evaporation. The double form shown in Figure 21.1 may be made easily. Three single hooks are adequate; the long arm of the hook goes on the outside.

Droppers

Short glass tubes, having the general form of a medicine dropper and fitted with a small rubber bulb on the large end, are useful for adding small volumes of liquid to a system. The short-tip form is usually available. If desired, long tips may be drawn easily.

Reaction Vessels

Our primary concern here is the material of which a reaction vessel is made. In the course of many analyses, the samples are subjected to one or more processes or operations. Broadly speaking, these steps must not result in any action with the container that will interfere with the desired determination. Several examples of undesired action on the container will illustrate the problem: (1) In determination of minute amounts of silica in water, some sodium silicate may be dissolved out of a glass container, thus increasing the silica value of the solution. (2) Hydrofluoric acid must not be measured in a glass graduate, since this acid attacks the glass. (3) Fusion of a sample with sodium carbonate in a porcelain crucible will often result in attack on the container, and will ruin both the container and the analysis. (4) Ignition of an alloy steel at 1200° will melt a glass combustion tube. (5) Mixed hydrochloric and nitric acids rapidly attack platinum ware.

Obviously, selection of a vessel or material for a particular analysis must be given serious consideration. No general coverage of the subject can be undertaken here. However, the conditions of experimentation must be such as to enable the analyst to measure that which is wanted without interference from the materials of the containing vessel.

Glass perhaps is the material used most widely for reaction vessels. Pyrex brand, borosilicate vessels are very popular, although soft flint glass is still important, especially for measuring vessels. Porcelain and several other refractories are employed extensively. For some purposes, platinum is almost indispensable; however, because of its cost, a cheaper

substitute is badly needed. Certain plastic materials are finding some use in special cases.

Wash Bottle

The wash bottle is one of the most characteristic objects to be seen in most analytical laboratories. The general form shown in Figure 21.2 is widely used. Various kinds of vessels serve, but glass Florence flasks are most common. Their capacity is usually 500 or 1000 ml.

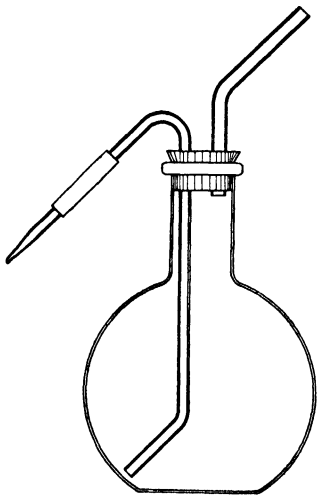


Figure 21.2

Form for student wash bottle.

In routine laboratories each analyst may have a wash bottle for hot water, for cold water, and for any special washing liquids to be used.

Various kinds of wash bottles are commercially available. Included are those of all-glass construction, those operated by squeezing a rubber bulb, those which do not "squirt" the first drop leaving the tip, those with special valves, and those made of polyethylene, the body of which is squeezed to force liquid out of the tip.

Each student should make a wash bottle according to the instructor's directions. In general, the following points should be followed: (1) fire polish the ends of the tubes; (2) make smooth bends, that is, avoid kinks and keep the bend in a plane; (3) make the long end of the mouthpiece about 12 to 15 cm long and cut the other end to come just below the underside of the stopper; (4) cut the upper end of the delivery tube about 3 cm below the bend; (5) make the tip about 8 cm long, and draw the exit end according to the N.B.S. form for pipets (see Figure 4.5, page 50); (6) attach the tip to the delivery tube with a piece of rubber tubing of a size to fit snugly.

Desiccator

A common form of glass desiccator is shown in Figure 21.3. Such containers are much used for keeping materials away from the outside atmosphere or in a controlled atmospheric environment. Crucibles heated to high temperatures are usually cooled to room temperature in a desiccator before they are weighed.

A desiccator is usually charged with some solid drying agent, such as anhydrous calcium chloride, barium oxide, phosphorus pentoxide, barium perchlorate (Dessichlora), magnesium perchlorate (Anhydrone), or calcium sulfate (Drierite). Solid potassium hydroxide is sometimes added to absorb carbon dioxide. Concentrated sulfuric acid may be used, along with a supply of glass beads to diminish splashing of the liquid when the desiccator is carried.

The efficiency of desiccants can be stated from two points of view. The amount of moisture that will be left in a closed space, containing incompletely consumed desiccant, is given by the vapor pressure of the desiccant.[1] The vapor pressure, accordingly, measures the extent to which the desiccant can remove water. A second factor is the amount (weight) of water that can be removed per unit weight of desiccant, i.e., the capacity of the desiccant. In general, substances that undergo primary chemical reaction with water, such as sodium metal and phosphorous pentoxide, have very low vapor pressure, but also low capacity. Substances such as magnesium perchlorate and calcium chloride, which form hydrates, have higher vapor pressures, but also greater capacities.

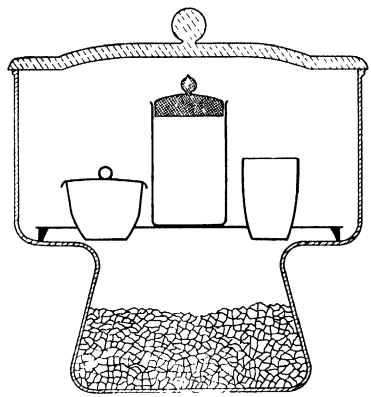


Figure 21.3

Desiccator.

For general student laboratory use, a desiccant of moderately low vapor pressure and high capacity is preferred; calcium chloride has long been a favorite. If the cost permits, a more efficient agent such as calcium sulfate is to be preferred. The student must remember that a substance cannot be dried in a desiccator containing a desiccant the vapor pressure of which is greater than that of the substance to be dried. Thus, freshly ignited calcium oxide should not be left for an appreciable time over calcium chloride unless the latter is fresh. A saving factor in the latter example is the relatively slow rate of hydration of the lime when it has been ignited at a very high temperature. The student must also remember to renew the desiccant whenever it shows signs of being spent, since its effectiveness may rapidly decrease to almost zero.

[1] Tables of the vapor pressure or relative vapor pressure of the commonly used drying agents may be found in handbooks and other reference works.

The desiccator cover should fit well on the ground joint. Enough lubricant, such as Vaseline, should be used on the joint to make the cover slide smoothly, but not so much that the cover will slide off if the desiccator is tipped somewhat in carrying. The cover may be manipulated by sliding it off and on. When very hot crucibles are placed in a desiccator, expanding air will cause the cover to "bump" at first. Then, as the air cools, a partial vacuum develops. The desiccator must then be opened by sliding the lid off.

Preferably a hot crucible should be allowed to cool well toward room temperature before being placed in the desiccator. Containers such as crucibles, holding residues to be weighed, should always be covered with lids to prevent the material in them from being swept out as the air rushes in when the cover of the desiccator is moved aside.

REAGENTS

The great majority of chemical reactions and transformations used in analytical processes require reagents of some kind. It is of first importance to know the reagent needed for a given purpose. Second only to this requirement is knowledge that the reagent has the desired degree of purity for the intended use.

Purity

In quantitative chemical analysis it is obviously very important to have reagents sufficiently free of interfering impurities that separations and measurements on the sample material will not be affected seriously. Since ordinary reagents are always contaminated to some extent, the analyst must keep in mind the nature of any possible interference and its probable magnitude. Thus, most distilled water contains at least traces of ammonia, but not enough to affect appreciably most determinations of nitrogen by the Kjeldahl titrimetric method. In determining ammonia in water, however, where the total may be less than 1 mg per liter, a specially distilled, ammonia-free water must usually be prepared.

The contamination of reagents may be traced to various sources. Very often chemicals purchased on the market do not have the required purity. In other cases, contaminating constituents are negligible. The analyst, as a disciple of Robert Boyle, should be a "skeptical chemist" in the case of reagents.[2] For exacting work T. W. Richards went so far as to maintain that one should assume that every reagent is impure until it is shown to be otherwise.

Many analytical chemicals are now commercially available in a reason-

[2] See Boyle, *The Skeptical Chemist,* Dutton, 1661.

ably satisfactory state of purity. Examples of such materials are the "Reagent Grade," "Analytical Reagent," and "Analyzed" products. The analysis of the substance is given on each bottle. Even so, precise work often necessitates purifying or testing many substances. Several books[3] provide general directions for such work and specific directions for reagents studied by the Committee on Guaranteed Reagents of the American Chemical Society.

The reagents furnished for student work in the quantitative laboratory are acceptable *except in special cases as noted.*

Standards

Chemicals of known purity or reactivity may be used as standards in terms of which to make measurements. Such substances were mentioned in Chapter 12 as primary standards in the discussion of titrimetry. In this type of measurement such primary standards are used for preparing a standard titrant or for standardizing a solution of unknown value.

A somewhat different application of standards is for checking the efficiency and reliability of an apparatus or a method of analysis. Thus, a common practice in steel analysis is to try the combustion apparatus with a sample of known carbon content. Many similar cases might be cited.

Water

The water used in analytical work presents a special problem in most cases. City water supplies usually carry so much dissolved matter that, unless they are treated, they cannot be used for this purpose. Distillation of water removes nonvolatile material; however, volatile constituents are carried along with the steam and dissolve, at least in part, in the condensed water. Thus, a supply of water that is "hard" because of dissolved calcium hydrogen carbonate may yield a distillate nearly saturated with carbon dioxide, with a *p*H near 5. Heating the raw water liberates the carbon dioxide according to the equation

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2\uparrow$$

Certain analytical work necessitates the use of a special still to remove such constituents. Increasing application is being made of purification apparatus containing ion-exchange materials through which the water is passed. Provision must be made, of course, for the removal of both

[3] Henderson and Fernelius, *Inorganic Preparations,* McGraw-Hill, 1935; Rosin, *Reagent Chemicals and Standards,* Van Nostrand, 1946; and Wichers *et al., Reagent Chemicals,* American Chemical Society, 1950.

cations and anions. Careful check must be kept on the effectiveness of the exchange process, for an exhausted column is of no value.

Distilled or deionized water is preserved and distributed preferably in a system in which the water comes into contact only with tin or aluminum.

Solutions

When water and many aqueous solutions, especially of the strong alkalies, are kept in glass containers, there is slow solvent action on the glass. Solutions of sodium or potassium hydroxide in soft glass show increase in basicity in the course of two or three weeks. After standing some weeks in glass, a solution of ammonia will contain numerous flakes of insoluble material. Also, insoluble deposits may form in other solutions, such as the phosphates. Whenever such deposits contain nonvolatile matter, any precipitates formed by means of the solutions will be contaminated and will weigh too much. These solutions should be filtered before use, unless it is known that the deposits are unobjectionable. In line with this discussion, the unforgivable act is for a student to go from bottle to bottle with his dirty pipet to withdraw solutions. Some solutions lose their effectiveness after standing too long. Thus, hydrogen peroxide decreases in oxidizing capacity, and titanous chloride decreases in reducing capacity.

Use of Chemicals

Many students seem to think that, if a little reagent works, more ought to work better. Even in the case of mass action effects, such a conclusion is not justified. In many cases too much reagent ruins the determination. In titrations with methyl orange indicator, for example, more than two drops of indicator solution makes the end point very uncertain.

Then, too, the problem of wastage is involved. Many chemicals are expensive. Consequently, it is economically desirable to use only the amount needed.

Occasionally a dangerous situation may arise from use of too much reagent. Apparatus may not be designed with a factor of safety large enough to stand serious overloading. Especially must this possibility be kept in mind for systems developing high pressures, such as calorimeter bombs.

OPERATIONS

In a laboratory for elementary work some rather general operations are done repeatedly. A few simple ones will now be described briefly.

Cleaning

Cleanliness is not always demanded in quantitative analysis, but in some processes and operations it is a strict necessity, e.g., in the use of burets and pipets to deliver liquids.

Specific directions are given in another place for preparing and using cleaning solutions for vessels that are used to deliver specified volumes of liquid. Open vessels, such as beakers, may be cleaned in the same way. More often with such containers it is advantageous to rub the moist surface with finely ground pumice stone. Subsequent thorough washing is necessary.

Although the use of clear, clean-looking glassware gives one confidence in the operator, the really important thing to know is that there is nothing present in the system to interfere with the obtaining of reliable results.

Cleaning platinum ware is a special problem; directions for this process are included in Chapter 28.

Drying

The term "drying" is not easily defined, since the nature of the operation may vary and the degree of dryness may have to be specified. Thus, one might dry sand by heating it to constant weight at 105°. In contrast, the removal of the last traces of water from 95 per cent ethanol is a very different operation. For present purposes, the term may be taken to mean heating at some specified temperature, such as 105°, or removal of water by causing it to react with some substance. As examples of the latter process, air may be dried by bubbling it through concentrated sulfuric acid, or diethyl ether may be dried by allowing it to stand for some time over clean metallic sodium.

Since a variety of solids, liquids, and gases may have to be dried, no attempt is made to suggest generally useful procedures. In selection of the process to be used, the chemical nature of the sample must be taken into account. In any case, one must be sure that only the desired reaction takes place. Thus, if coal is dried in an ordinary oven at 110°, something more than water will be evolved.

The specific operation of drying precipitates for subsequent weighing is discussed in Chapter 28.

Evaporation

Evaporative operations are used to remove part or all of a volatile liquid from a system. The objective may be to concentrate a solution

by expelling part of the solvent, or it may be to remove the liquid entirely. The process in mind here is one aspect of the more general problem of separation by volatilization discussed in Chapter 7.

The means employed depend upon the properties of the system and the facilities available. Gas burners serve for boiling a solution in a vessel such as a beaker. Spattering may result from too violent heating. Often superheating results in troublesome bumping, which may cause loss of material. Such action may be reduced or avoided at times by adding "boiling tubes" (glass tubing drawn to fine bore, cut off to lengths of several inches and sealed at one end). Pieces of platinum, unglazed porcelain, or carborundum also serve.

Gas or electric hot plates are much used in evaporation processes. Some have a layer of sand to aid in producing more even heating. Steam baths or high-pressure steam hot plates are useful. They give somewhat slower heating but rarely cause spattering or bumping of a solution.

In all such work the liquid in the container should be protected from foreign material by some cover, such as a watch glass. This cover should be slightly above the rim of the container, to facilitate escape of the volatile constituent.

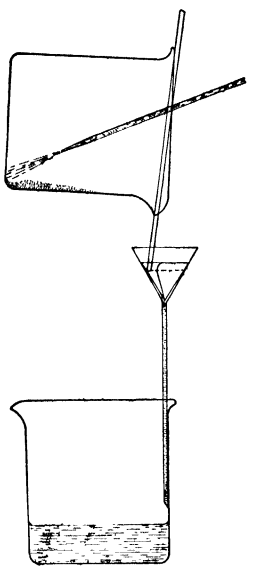


Figure 21.4

Transfer of a solution and precipitate.

Transfer of Liquids

The method and care used by a student in transferring liquids indicate, in considerable measure, his attention to manipulative details. Since our subject is quantitative analysis, it should be obvious that a solution of the desired constituent must be handled with meticulous care. The loss of a single drop from a total of 50 ml is an error, in this operation alone, of nearly 0.1 per cent of the volume involved. This value is the limit of total error within which we should like to hold the whole procedure for good work.

When a liquid is poured from a beaker or casserole with a lip, a small amount is likely to run down the outside of the vessel under the lip. This results in loss of solution, of course. Such loss may be prevented by placing a stirring rod in contact with the lip of the vessel and then pouring the liquid down the rod. The operation is illustrated in

Figure 21.4. In addition, the figure shows a way of holding the beaker, the rod, and the wash-bottle tip when transferring a solution and precipitate from the beaker to a funnel. The position shown for the funnel (against the wall of the lower beaker) prevents droplets from falling to the solution below and spattering out of the beaker.

Glass-working

Successful glass-working may be summarized as doing the right thing, in the right way, at the right time, with the right material. The operation as a whole is very much an art, all but the simplest steps usually requiring long and patient practice for the development of proficiency.

For the simple equipment required in elementary quantitative analysis, one needs only to cut, bend, and fire-polish tubing and rods. Sealing stopcocks on burets, re-drawing pipet and buret tips, etching graduation marks on flasks, and similar operations represent the next level of difficulty.

If students have not had enough prior training to do the few operations described above, the instructor should demonstrate them. Such a demonstration is very valuable for teaching of technics, such as glass-working.

LABORATORY HAZARDS

In one way or another many common laboratory processes and operations are potential sources of danger. Occasionally a textbook writer includes some word of caution for a specific situation, such as evaporation of perchloric acid in the presence of organic matter. He cannot be expected, however, to repeat on every page that poisonous liquids should not be sucked by mouth into pipets.

Any competent and conscientious instructor is alert to such hazards. Even so, safety must be emphasized at all times. One cannot repair Humpty-Dumpty after an explosion has blown the top of a calorimeter bomb through his forehead (which, incidentally, can happen).

In the laboratory first-aid kits should be available, so that simple measures may be taken in case of accident.

Cuts and Burns

In the quantitative laboratory cuts arise most frequently from the usual incautious handling of glass. Burns are caused by hot objects or by chemicals. The latter type include especially burns from acids such as nitric, sulfuric, and hydrofluoric. The hot, concentrated sulfuric acid in a Kjeldahl digestion flask is always a danger. Action of hydrofluoric

acid on the skin is particularly to be avoided. The usual first-aid treatments for cuts and burns should be used.

Explosions

Under this heading are included various kinds of more or less violent reactions. Thus, carelessly mixed water and hot, concentrated sulfuric acid may spatter badly. Improperly neutralized sulfuric acid in a Kjeldahl nitrogen determination may squirt out of the neck of the flask with enough force for the solution to hit the ceiling of the laboratory. In contrast, perhaps, the bursting of a calorimeter high-pressure bomb may be classified as a real explosion. Any container under high internal pressure, such as a gas cylinder, is a possible explosion hazard.

About the only suggestion in regard to general explosions that can be stated briefly is that any local situation should be examined carefully. If such danger is inherent in the method or apparatus, directions should be followed faithfully and every known care exercised. If laboratory rules call for safety glasses and protective shields, they should be used.

Poisons

Most chemicals in the laboratory are essentially poisonous to the human body. Perhaps here as much as anywhere chemists demonstrate the soundness of the old adage, "familiarity breeds contempt."

Poisons in the solid state are probably least dangerous as one uses them in the laboratory. Even so, it is usually best not to come into direct contact with them.

With liquids, there is the danger of breaking containers and splashing the material in handling. Sucking a solution into a pipet is hazardous. Some laboratories require the use of rubber bulbs or other devices for this operation.

Some gases, such as hydrogen sulfide, are *very* poisonous. Fortunately, this compound is easily recognized by its odor, even in very low concentrations. Mercury vapor, however, is not, and its effects are cumulative. The oxides of nitrogen evolved in dissolving brass in nitric acid are very poisonous. Gases such as the halogens react on the respiratory system, and hydrofluoric acid vapor attacks the eyes.

CHAPTER 22

EXPERIMENTAL DATA

Every quantitative determination includes the acquisition and use of experimental data. This aspect of the analytical procedure concerns the figures in students' notebooks. The recording and handling of these data may be a very simple matter, as in many routine industrial determinations; or it may be fairly complicated, as in the establishment of research methods which involve simultaneous equations and control charts. In this chapter, then, some of the most significant items relating to such analytical data are summarized.

THE LABORATORY NOTEBOOK [1]

The ability to prepare an adequate and reliable record of the results obtained in an analysis is a fundamental requirement for a successful experimental worker.

The record books employed in different laboratories differ greatly.[2] Permanently bound books are usually recommended. In some books the frequently recurring entries are printed, with blank spaces left for entering experimental results and variable items. Much more frequently the book consists entirely of blank pages. It is for the latter type of notebook that the suggestions to follow are included.

Likewise, there is no uniformity in record books regarding the form to be followed in preparing a report. Two points of prime importance in entering the data are the arrangement to use and the specific items to include. Since different kinds of measurements involve different specific items, we may expect variations in this direction. There are often other points of difference. In any case, however, the general requirement of a report considered satisfactory from the standpoint of uniformity

[1] The material in this section is based on the notebook by Mellon, *Quantitative Analysis Record Book,* Crowell, 1944.

[2] See *J. Chem. Educ.* 10, 403 (1933), for a report of a symposium on laboratory notebooks, records, and reports.

may be summarized in a single statement: At any time another analyst should be able to determine easily from the record what was done and how the information was obtained. The analyst's notebook should be a clear and complete revelation to anyone "skilled in the art."

Data Required

In order for the book to meet this test, the record should contain entries covering the following items: (1) date of determination; (2) description of the sample, including some designation such as a serial number or other distinguishing mark; (3) name or formula of the constituent measured, or the name of the property measured, including the kind of material examined; (4) method of determination used, including two references to sources of directions; [3] (5) amount of sample taken, except when it does not have to be measured; (6) readings for the measurement of the desired constituent or property; (7) amount of the desired constituent found, expressed in appropriate terms; [4] and (8) the signature or initials of the analyst.

CHEMICAL REACTION

$$2\ HCl + Na_2CO_3 \rightarrow 2\ NaCl + H_2O + CO_2\uparrow$$
$$2(36.46)\ g\ HCl \simeq 106.00\ g\ Na_2CO_3$$

CALCULATION

$$1\ ml\ HCl \simeq 0.009317\ g\ Na_2CO_3$$

$$\%\ Na_2CO_3 = \frac{\text{vol.} \times \text{titer} \times 100}{\text{g sample}}$$

$$= \frac{40.20 \times 0.009317 \times 100}{0.4500}$$

$$\begin{aligned} \log 40.20 &= 1.60423 \\ \log 0.009317 &= 7.96928 - 10 \\ \log 100 &= 2.00000 \\ &= 11.57351 - 10 \end{aligned}$$

$$\begin{aligned} \log 0.4500 &= 9.65321 - 10 \\ \log \text{percentage} &= 1.92030 \\ \text{percentage} &= 83.23 \end{aligned}$$

$$\%\ Na_2O = \%\ Na_2CO_3 \times \frac{Na_2O}{Na_2CO_3}$$

[3] The first reference should be the textbook that is being followed. The items should include author, title, page, and year, e.g., Mellon, *Quantitative Analysis*, p. 225, 1955.

[4] Frequently analysts determine physical properties, such as density, which involve no calculation of the amount of a constituent.

All of this information should be placed on the right-hand pages of a blank book, preferably in plain slant or vertical lettering. In addition, the preceding *left*-hand pages should carry the chemical equations for all the essential chemical reactions of the procedure, together with a sample calculation (preferably using logarithms with four or five places) to show that the correct method was followed. If desired, brief notes may be added to indicate any special items that should come to the attention of the one who is to inspect the report.

The accompanying examples show typical entries for a titrimetric and a gravimetric determination.

Expression of Results

Several different bases are in current use for expressing analytical results. Some of these are parts per million, parts per hundred thousand, milligrams per liter, grams per hundred milliliters, milligram per cent, percentage by volume, and percentage by weight. Still others, of limited application, are employed industrially. Percentage by weight has been adopted most widely and should be used unless another basis is specified.

In using the percentage system, distinction should be made between per cent and percentage error. Suppose that 90.00 per cent is the most probable value for the amount of silver in an alloy, and that the student

Sample: SA 31 3/20/55

ALKALINITY OF SODA ASH

Titration with HCl in presence of modified methyl orange indicator.
R. 1: ASTM Standards **7,** 618 (1952)
R. 2: Mellon, "Quant. Anal." page 405 (1955)

Sample wt:	I	II
Container + S.	20.5841	20.1341
Container	20.1341	19.6879
Sample	0.4500	0.4462
Constituent det'd:		
HCl $T_{(Na_2CO_3)}$ = 0.009317 g		
Vol. used, final	40.20	39.80
Vol. used, initial	0.00	0.00
Ml	40.20	39.80
G Na_2CO_3	0.3745	0.3708
% Na_2CO_3	83.23	83.12
Ave. % Na_2CO_3	83.2	
% Na_2O	48.7	

Richard Roe

obtains a value of 89.50 per cent. The difference, 0.50, represents the error, in per cent. Some refer to it as the *absolute* error. The percentage, or *relative,* error, is obtained by dividing the error by the most probable value and multiplying by 100. In the example cited, this error is 0.55 per cent.

Recommended Forms for Reports

In order to assist in the preparation of acceptable reports in a blank-page book, typical records are included to illustrate how such information may be handled efficiently.[5] Although these sample records are limited to gravimetric and titrimetric processes, a semester's experience with these two kinds of methods should enable the student, with a little thought, to adapt the fundamental requirements to new situations.[6]

CHEMICAL REACTIONS

$$Zn^{+2} + HPO_4^{-2} + NH_4^+ + OH^- \rightarrow ZnNH_4PO_4 \downarrow \ldots$$

$$2\ ZnNH_4PO_4 \xrightarrow[900^\circ]{\Delta} Zn_2P_2O_7 + 2\ NH_3 \uparrow + H_2O \uparrow$$

CALCULATION

$$\text{Factor} = \frac{2\ Zn}{Zn_2P_2O_7} = \frac{130.76}{304.72} = 0.4291$$

$$\%\ Zn = \frac{\text{residue} \times \text{factor} \times 100}{\text{sample}}$$

$$= \frac{0.4153 \times 0.4291 \times 100}{1.0015}$$

$$\log 0.4153 = 9.61836 - 10$$
$$\log 0.4291 = 9.63258 - 10$$
$$\log 100 = \frac{2.00000}{1.25094}$$

$$\log 1.0015 = \frac{0.00065}{1.25029}$$
$$\log\ \%\ Zn = 1.25029$$
$$\%\ Zn = 17.79$$

[5] The author's *Quantitative Analysis Record Book* contains additional forms selected to cover several commonly used methods: the calibration of flasks, pipets, and burets; three procedures for the preparation of standard titrants; the use of such solutions for direct and back titrations; and two simple gravimetric determinations. In the different forms some variation is shown to illustrate common preferences. Thus, the titrimetric calculations cover titrant values which are expressed in terms of normality or titer. Samples for analysis are shown as having been weighed by difference from a container or directly on counterpoised glasses. Sample calculations are shown, first in simplest form and alternatively in "factor-label" form. One needs no sample calculation if a factor-weight amount of sample is used.

[6] Other types of records may be found in Arenson and Rieveschl, *Laboratory Notebook for Introduction to Quantitative Analysis,* Crowell, 1944; and Engelder, *Laboratory Record Book of Quantitative Analysis,* Wiley, 1938.

Rules

In entering analytical data in the record book, in accordance with the forms proposed, the student should, unless otherwise directed, conform to the following rules:

1. Enter all records in ink. Measurements should be recorded directly in the book *as soon as they are read.* Do not use loose scraps of paper for recording data.

2. Before an exercise is begun, fill out all headings as far as experimental work permits.

3. In recording measurements where subtractions are to be made, place the smaller value underneath the larger whenever possible, whether the latter is obtained first or last.

4. Use the proper number of significant figures and include the intended zeros. Thus, a volume of 30.00 ml should not be recorded as 30 ml.

Unless otherwise directed, calculate percentages as far as the third decimal place and round off to the second. In reporting the average of two or more determinations, calculate the result to one decimal place if the difference between the extremes is more than 0.1 per cent and to two decimal places if the difference is 0.1 per cent or less. (When this principle of calculating averages to only one uncertain figure is applied to very small amounts of constituents, more than two decimals will be necessary.)

Sample: 301B 4/10/55

ZINC IN BRASS

Zn in filtrate from Cu pptd. with $(NH_4)_2HPO_4$ as $ZnNH_4PO_4$ and ignited in Gooch xbl. to $Zn_2P_2O_7$
R. 1: Furman, "Scott's Std. Meth. Anal.", I, 1059, 1084 (1939).
R. 2: Fales and Kenny, "Inorg. Quant. Anal.", p. 52 (1939).

		I	II
Sample wt:			
By counterpoise		1.0015	1.0003
Constituent detd.:			
Xbl. + $Zn_2P_2O_7$	1)	~~12.6555~~	~~12.4393~~
	2)	~~12.6545~~	~~12.4382~~
	3)	12.6543	12.4381
	4)		
Crucible	1)	~~12.2391~~	~~12.0241~~
	2)	12.2390	12.0243
$Zn_2P_2O_7$		0.4153	0.4140
Zn		0.1782	0.1776
% Zn		17.79	17.75
Ave. %		17.77	
			M.G.M.

5. Do not make erasures nor detach pages. If a report is ruined or an exercise is repeated, draw a line diagonally across the page and begin a new record upon the next blank page.

6. Do not put data for more than one determination on a page.

Number of Determinations

At least two determinations of the desired constituent should be made on each sample in order to obtain an average value. Whenever possible, the operations of these two determinations should be carried along together. The report should show the value obtained for every determination completed, as well as the average for the two or more that are to be submitted. The average may be based on the closest-checking pair, if there is adequate basis for such selection. In case of uncertainty, the textbook and instructor should be consulted.[7]

ERRORS AND RELIABILITY OF DATA[8]

In experimental work, such as that involved in obtaining quantitative chemical data, an operator uses two kinds of numbers. These may be distinguished as *counting* and *measuring* numbers. Analysts should recognize certain characteristics of each kind.

Counting numbers are those which represent how many of a given item are concerned. Thus, a lecture room may contain 200 seats, and a laboratory 50 analytical balances. If care is taken in making such counts, there can be no question as to the reliability of the results. Each individual making the count should obtain the same number.

Measuring numbers are those obtained in the course of determining the magnitude of some physical property, such as length, volume, or mass. Essentially, the process consists in finding the number of times a given standard goes into the unknown being measured.

It is common experience that such a measurement may yield different values if it is made by different individuals, by the same individual with different methods, or even by the same individual when he repeats the process with the same method. Conditions of measurement affect the results, of course.

Probably all who are competent enough to handle a surveyor's 100-ft. tape could agree that a football field is three tape-lengths long. In contrast, if a fraternity initiation committee could think of no more constructive conditioning for pledges than to have each of a dozen of

[7] Processing and grading of reports are treated in the author's *Quantitative Analysis Record Book.*

[8] For a more extended discussion, see Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis,* Ch. 15, Macmillan, 1952.

them measure the same distance (but obviously not the known football field) by laying end-to-end a 1-in. measure, the results would probably show considerable variation. The various difficulties that would be likely to contribute to this variability of the results are obvious. This simple example may be taken as illustrative of what the analyst must be on the alert to evaluate whenever a quantity, such as an atomic weight, a density, or an electrical potential, is determined experimentally. Some uncertainty, whether small or large, is likely to be associated with the result. The density of water at different temperatures is commonly given (in tables) to as many as seven decimal places, but the atomic weight of ruthenium approved by the International Committee is 101.1. In these two cases there must be a wide difference in the degree of certainty of the results.

Definitions

The general subject of experimental results and their nature is of great importance in any field such as quantitative chemical analysis, in which the factual data rest upon physical measurements. The meanings of a few terms, as used in this connection, should be kept in mind.

A *true value* is one about which there is no question of uncertainty. In experimental work such certainty can be associated only with counting numbers, such as the number of burets which one has to calibrate. With measuring numbers we can know a value only within the limits of the method of measurement used, the range of uncertainty being a function of the overall refinement of the measurement. For the atomic weight of ruthenium, for example, we know the value as yet to a certainty of barely one part in a thousand.

A *most probable value* is a measuring number which is the result of experimental determination. Presumably, it applies only to data obtained by the use of the most refined methods available and by the most careful attention to the attendant operative details. Perhaps the best example of most probable values used by chemists is the table of atomic weights. Each value therein (except oxygen, which has the arbitrarily assigned value of 16.0000) has been selected by the International Committee as being the best thus far obtained. Another example is the report issued by the National Bureau of Standards for each of its analyzed samples. In the analysis of these very carefully prepared materials, usually at least ten skilled analysts determine a given constituent by one or more well-tested methods. On the basis of all the reports, the Bureau recommends a value, which may be considered the most probable value for the experimental conditions maintained.

TABLE 22.1

ANALYSIS OF STANDARD SAMPLE 153: COBALT-MOLYBDENUM-TUNGSTEN STEEL*

(In per cent)

	C	*Mn*	*P*	*S*		*Si*	*Cu*	*Ni*	*Cr*	*V*	*Mo*		*W*		*Co*
Analyst†	Direct combustion	Persulfate-Arsenite	Alkali-Molybdate	Gravimetric (direct oxidation and precipitation after reduction of iron)	Combustion	Nitric-hydrochloric acid dehydration	H_2S-CuS-CuO	Weighed as nickel dimethylglyoxime	$FeSO_4$-$KMnO_4$ titration	HNO_3 oxidation, potentiometric titration in presence of tungsten	Gravimetric	Colorimetric	Gravimetric	Colorimetric	Zinc oxide-alpha-nitroso-beta-naphthol
1	0.864	.220[a]	.027[b]	0.010	—	.189[c]	0.097	0.101	4.13[d]	2.05	8.37[e]	—	1.60[f]	—	8.47
2	.860	.227[a]	.025	009	0.010	176[c]	.091[g]	.096[h]	4.12	2.02[i]	8.41[j]	8.44	1.61[k]	—	8.44
3	.868	.219[a]	.027	—	.007	.181[c]	.103[l]	.093	4.17	2.04	8.37	8.37	—	1.58[m]	8.52
4	.870	.222[n]	.024	.006	.007[o]	.176	.098[l]	101[p]	4.13[q]	2.05	8.30[j]	8.35	1.57	1.54[m]	8.41
5	.866	.22[a]	.023[r]	.008	.010[s]	180	090[t]	.107[h]	4.12[u]	2.04[v]	—	8.35	1.60[f]	1.60[m]	8.47
6	—	.214[w]	—	—	.010	.195	—	.12[l]	4.16	2.00	8.36[x]	8.36	—	1.60[y]	8.54[z]
7	.860	.225[a]	.025	—	.011[o]	.198	.098[aa]	.116	4.16	2.02	8.40[ab]	—	1.57[f]	—	8.40[l]
8	.863	.21[a]	.025	—	.008	.200[ac]	.11[ad]	.117[h]	4.13	2.05[ae]	8.40[ab]	—	1.55[k]	—	8.40
9	.863	.212[af]	.025	—	.011[s]	.19[e]	.108[ad]	.11[h]	4.13	2.08	8.42[e]	8.45	—	1.58[m]	8.41
AV.	0.864	0.219	0.025	0.008	0.009	0.187	0.099	0.107	4.14	2.04	8.38	8.39	1.58	1.58	8.45

* Reproduced with permission of the National Bureau of Standards.

[a] ZnO separation.

[b] Tungsten removed by digestion in HCl–HNO_3. Phosphorus precipitated with molybdate in hot nitric acid solution and ultimately weighed as $Mg_2P_2O_7$ after removal of arsenic.

[c] Double dehydration with perchloric acid.

[d] Persulfate oxidation, potentiometric titration with ferrous ammonium sulfate solution standardized with recrystallized potassium dichromate.

[e] Alpha-benzoinoxime method after removal of tungsten by acid digestion. Corrected for molybdenum occluded in tungsten, and the main molybdenum precipitate corrected for ammonia insoluble and tungsten. See BS J. Research 9, 1 (1932) RP453.

[f] Single precipitation by acid digestion and cinchonine. Tungsten corrected for silicon, iron, chromium, vanadium, and molybdenum.

[g] H_2S—colorimetric method.

[h] Glyoxime precipitate titrated with cyanide.

[i] Ferrous sulfate titration with $K_3Fe(CN)_6$ indicator.

[j] H_2S–MoO_3 method.

[k] Double precipitation by acid digestion and cinchonine.

[l] Finished by electrolysis.

[m] Hydroquinone colorimetric method.

[n] Periodate-colorimetric method.

[o] SO_2 absorbed in starch-iodide solution and titrated with KIO_3 solution.

[p] Glyoxime-electrolytic method.

[q] Chromium oxidized with $KClO_3$.

[r] Tungsten, chromium and molybdenum removed, phosphorus determined by the molybdenum blue-photometric method.

[s] Sulfur gases absorbed in NaOH–H_2O_2 solution and excess NaOH titrated with H_2SO_4.

[t] Thiocyanate precipitation, thiosulfate titration.

[u] Chromium oxidized with $HClO_4$ and titrated with ferrous ammonium sulfate by using orthophenanthroline indicator. Corrected for partial oxidation of manganese and cobalt.

[v] Solution from titration of chromium (footnote u) titrated with 0.05–N $KMnO_4$.

[w] Chromium and cobalt removed by treatment with NH_4OH and $(NH_4)_2S_2O_8$.

[x] Molybdenum precipitated with H_2S, reduced with zinc, and titrated with $KMnO_4$.

[y] $SnCl_2$–thiocyanate colorimetric method.

[z] NaOH–ether–cupferron–electrolytic method.

[aa] Precipitated with $Na_2S_2O_3$, finished by electrolysis.

[ab] H_2S–alpha benzoinoxime method.

[ac] Double dehydration with HNO_3 and H_2SO_4.

[ad] Copper precipitated first with H_2S, then precipitated with alpha-benzoinoxime in ammoniacal solution.

[ae] Ferrous sulfate-$KMnO_4$ titration method.

[af] Chromium volatilized as CrO_2Cl_2.

†LIST OF ANALYSTS

1. Ferrous Laboratory, National Bureau of Standards. John L. Hague in charge. Analysis by J. P. Hewlett, Jr.
2. E. B. Welch, Firth-Sterling Steel Co., McKeesport, Pa.
3. Daniel Harmon, Allegheny Ludlum Steel Corporation, Dunkirk, N. Y.
4. W. L. Emerson, The Cleveland Twist Drill Co., Cleveland, Ohio.
5. O. L. Van Valkenburgh, Crucible Steel Company of America, Halcomb Steel Division, Syracuse, N. Y.
6. T. R. Cunningham, Union Carbide and Carbon Research Laboratories Inc., Niagara Falls, N. Y.
7. W. F. Lantz, Bethlehem Steel Co., Bethlehem, Pa.
8. J. C. Sloss, Vulcan Crucible Steel Co., Aliquippa, Pa.
9. P. W. Rush and J. Cooperman, Universal-Cyclops Steel Corporation, Universal Division, Bridgeville, Pa.

The steel for the preparation of this standard was furnished by the Cleveland Twist Drill Co.

WASHINGTON, October 17, 1945

E. U. CONDON, *Director*.

Table 22.1 shows the various results obtained and reported for the analysis of Standard Sample No. 153 of the National Bureau of Standards. At the bottom of each column is the average, which is the recommended value.

Error refers to the deviation of a given value from some other value taken as a basis of reference. Ideally, this reference value for measuring numbers would be the most probable value. Actually, a more realistic value, at least in terms of determinability in some given laboratory, would be one obtained by the best analyst in the group, working under carefully controlled conditions.

Accuracy is an expression of the quality of a value. Numerically, it is a measure of the magnitude of the error. Suppose an analyst obtains 29.97 per cent for an N. B. S. sample stated to contain 30.00 per cent. The *absolute* error is 0.03 per cent ($30.00 - 29.97 = 0.03$). The *relative* error is 0.1 per cent ($0.03/30.00 \times 100 = 0.1$), or one part per thousand. In most ordinary analytical determinations results accurate to 0.1 per cent of the amount of the constituent measured represent a reasonably practical ideal, if (a) the method is satisfactory, (b) the analyst is competent and conscientious, and (c) the sample is homogeneous and stable. However, many thousands of industrial determinations are made in which the accuracy falls within the range of 0.5 to 5 parts per hundred of the constituent measured. In contrast, most of the atomic-weight values have an uncertainty of much less than one part per thousand.

Precision is an expression of the limits of variation or reproducibility of a value. A closely agreeing, or concordant, series of values is said to be precise. An example of good precision in ordinary analytical work would be the three buret readings, 22.20, 22.22, and 22.21 ml, for three titrations on a given sample. Low precision is illustrated by the three values, 40.5, 41.0, and 41.5 per cent, for three determinations of the volatile combustible matter in coal. In the latter case, the method is recognized as being incapable of high precision.

The student must not be misled into concluding that two (or more) closely checking, successively determined values insure accuracy. The same errors may simply have been repeated. The conclusion would have to be substantiated by checking with at least one entirely different, and equally reliable method. Practice does not necessarily make perfect.

Nature of Errors

A practical problem in obtaining physical data experimentally, and in using the results, involves recognition of the kinds and sources of errors.

The results may have been obtained by a single observer with one instrument; or they may be subject to variations that can arise from the practices of different observers, using different methods and different instruments. In any case, repeated measurements cannot be expected to yield results that agree exactly. The most expert pistol marksman does not hit the exact center of the bull's-eye a dozen times in succession at 100 yards.

Determinate errors. Errors that are constant and persist from one determination to another are known as *determinate errors.* Since the source of error is known, the value can be more or less closely estimated. Determinate errors may be instrumental in nature, e.g., inaccuracy in the graduation of a volumetric measuring vessel. Personal errors are due to peculiarities of the observer, such as defective color vision which may interfere with the detection of visual end points in titrations. Errors of method, such as contamination of a precipitate, failure to maintain compensating conditions, and faulty sampling, are examples of determinate error.

Determinate errors may be minimized in most cases by a recognition of their source and by the application of suitable precautions in the course of an analysis. In certain instances they may be determined directly and the necessary correction applied. Thus, all measuring instruments, such as weights and volumetric ware, can be calibrated. A blank determination may be made to determine the magnitude of the effect of impurities in the reagents. An indirect procedure which is used in many cases consists in making the complete determination on a known amount of constituent under conditions as nearly as possible like those to be encountered in the determination of approximately the same amount of constituent in an unknown sample. This standardization of method may be applied to such factors as concentration of reagents, temperature, and other routine items of procedure.

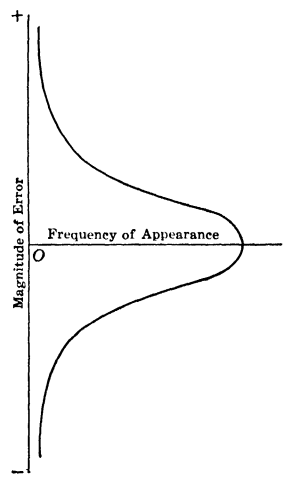


Figure 22.1

Probability curve.

Indeterminate errors. Errors that are accidental and beyond the control of the observer are called *indeterminate errors.* They are attributable to slight variations that occur in the course of successive observations.

The magnitude and sign of such errors follow the law of chance, as illustrated in the probability curve shown in Figure 22.1. An inspection of this curve shows the following points: (1) large errors occur less frequently than small ones; (2) very large errors are relatively unlikely to occur; and (3) positive and negative errors of the same numerical magnitude are equally likely to occur.

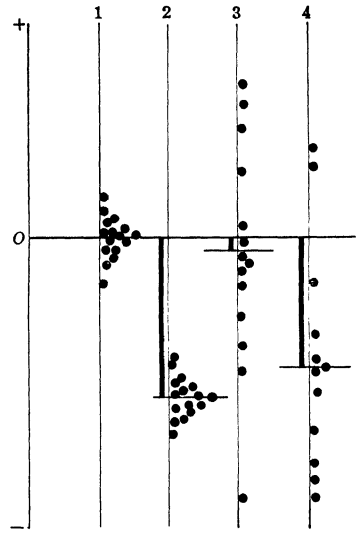


Figure 22.2

Effect of accidental and constant errors.

Figure 22.2 shows the effect of accidental and constant errors for a given determination made by four different methods.[9] Each dot represents a separate measurement. The long horizontal line represents the most probable value and the short horizontal lines represent the arithmetical means of each series. In series 1 and 2 the accidental errors are small and the values in either series agree closely among themselves, i.e., they show a good degree of precision. The accidental errors in series 3 and 4 are large. They do not agree well, as shown by their low degree of precision. Methods used for series 3 and 4 are impractical because a large number of observations would be necessary to establish a reliable mean. Methods used for series 1 and 2 are satisfactory in this respect. Series 2, however, shows a negative error of considerable magnitude, represented by the difference between the mean and the most probable value.

ARITHMETICAL CONVENTIONS

In the general handling of numerical data various conventions are usually followed by mathematicians, scientists, and technologists. A brief statement of two recommendations is included here.

Rejection of an Observed Value

If any given value is known to be in error because of accident, mistake, or other recognized reason, it should be rejected, of course, and not included in the calculation of an average or any other derived value.

[9] Benedetti-Pichler, *Ind. Eng. Chem., Anal. Ed.* **8**, 373 (1936).

In any such case, the record book should carry a notation of the rejection and the reason therefor.

In a series of results, however, frequently at least one value stands out as improbable in comparison with the evident consistency of the others. The question arises as to whether it may legitimately be rejected before the others are evaluated. One often-quoted rule is said to rest on sound mathematical reasoning. According to this rule, if at least four results are in a series, one may omit the suspected value temporarily and calculate the mean and the average deviation from the mean for the values retained. Then, if the deviation of the suspected value from the mean is at least four times the average deviation for the values retained, the suspected value should be rejected.

As an example, we may refer to Table 22.2, page 374. If a questionable result, such as 9.30, were included, its deviation from the average, 9.50, would be 0.20. Since this difference exceeds four times the average deviation, 0.038, the questionable result would be rejected on the basis of this rule.

Another basis is to reject a value if it is at least three times the standard deviation. For the data in Table 22.2 this product is 0.138 (3×0.046) if n is taken as 10 to calculate σ. The product is less than the deviation of the questionable result.

Several criteria for the rejection of observations have been compared recently.[10]

It may be noted that among quality control statisticians there is a tendency to retain all values, no matter how divergent individual values may appear.

Significant Figures[11]

One of the principles of handling the data of physical measurements is that a numerical result by itself should give an approximate idea of the precision of the value. This is indicated by the number of significant figures used in expressing the value. If there are fewer or more significant figures than are warranted, one may obtain an impression nearly as erroneous as from an inaccurate value.

The following definitions and rules are suggested by those given in Goodwin's book.[12]

A *number* is an expression of a quantity.

[10] Blaedel, Meloche, and Ramsay, *J. Chem. Educ.* **28**, 643 (1951).

[11] The material quoted in this section is reproduced with permission from Hamilton and Simpson, *Calculations of Analytical Chemistry*, McGraw-Hill, 1954.

[12] *Elements of the Precision of Measurements and Graphical Methods*, McGraw-Hill, 1920 [Author].

A *figure,* or *digit,* is any one of the characters 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, which, alone, or in combination, serves to express numbers.

A *significant figure* is a digit which denotes the amount of the quantity in the place in which it stands. In the case of the number 243, the figures signify there are two hundreds, four tens, and three units. They are therefore all significant. The character 0 is used in two ways. It may be used as a significant figure, or it may be used merely to locate the decimal point. It is a significant figure when it indicates that the quantity in the place in which it stands is known to be nearer zero than to any other value. Thus, the weight of a crucible may be found to be 10.603 g, in which case all five figures, including the zeros, are significant. . . .

By analysis, the weight of the ash of a quantitative filter paper is found to be 0.00003 g. Here the zeros are not significant but merely serve to show that the figure belongs in the fifth place to the right of the decimal point. . . . The same is true of the value 356,000 inches, when signifying the distance between two points as measured by instruments which are accurate to three figures only. The zeros are not significant. In order to avoid confusion, this value should be written 3.56×10^5 inches. If the distance has been measured to the nearest 100 inches, it should be written 3.560×10^5 inches.

Rule 1. Retain as many significant figures in a result and in data in general as will give only one uncertain figure. Thus, the value 25.34, representing the reading of an ordinary 50-ml buret, contains the proper number of significant figures, for the digit 4 is obtained by estimating an ungraduated scale division and is doubtless uncertain. Another observer would perhaps give a slightly different value for the buret reading, as 25.33 or 25.35. All four figures should be retained.

Rule 2. In rejecting superfluous and inaccurate figures, increase by 1 the last figure retained if the following rejected figure is 5 or over. Thus, in rejecting the last figure of the number 16.279, the new value becomes 16.28.

Rule 3. In adding or subtracting a number of quantities, extend the significant figures in each term and in the sum or difference only to the point corresponding to that uncertain figure occurring farthest to the left relative to the decimal point.

For example, the sum of the three terms 0.0121, 25.64, and 1.05782, on the assumption that the last figure in each is uncertain, is 26.71.

Rule 4. In multiplication or division, the percentage precision of the product or quotient cannot be greater than the percentage precision of the least precise factor entering into the computation. Hence, in computations involving multiplication or division, or both, retain as many significant figures in each factor and in the numerical result as are contained in the factor having the largest percentage deviation. In most cases, as many significant figures may be retained in each factor and in the result as are contained in the factor having the least number of significant figures.

For example, the product of the three terms, 0.0121, 25.64, and 1.05782,

on the assumption that the last term in each is significant, is

$$0.0121 \times 25.6 \times 1.06 = 0.328$$

for, if the first term is assumed to have a possible variation of 1 in the last place, it has an actual deviation of 1 unit in every 121 units, and its percentage deviation would be $(1/121) \times 100 = 0.8$. Similarly, the percentage deviation of the second term would be $(1/2564) \times 100 = 0.04$, and that of the third term would be $1/105782) \times 100 = 0.0009$. The first term, having the largest percentage deviation, therefore governs the number of significant figures which may properly be retained in the product, for the product cannot have a percentage precision greater than 0.8 per cent. That is, the product may vary by 0.8 part in every hundred or by nearly three parts in 328. The last figure in the product as expressed with three significant figures above is therefore doubtful, and the proper number of significant figures has been retained.

Rule 5. Computations involving a precision not greater than one-fourth of 1 per cent may be made with a 10-inch slide rule. For greater precision logarithm tables or other means should be used. . . .

Rule 6. In carrying out the operations of multiplication or division by the use of logarithms, retain as many significant figures in the mantissa of the logarithm of each factor as are properly contained in the factors themselves under Rule 4.

Thus, in the solution of the example given under Rule 4, the logarithms of the factors are expressed as follows:

$$\begin{aligned} \log\ 0.0121 &= 8.083 - 10 \\ \log\ 25.64 &= 1.409 \\ \log\ 1.05782 &= 0.024 \\ \hline & 9.516 - 10 = \log 0.328 \end{aligned}$$

EVALUATION OF DATA

As far as their sources are known, and to the extent that their magnitude justifies the effort, determinate errors may be estimated and correction made therefor. Often it is more feasible experimentally to compensate them by the selection of suitable working conditions. In any case, the obvious general approach is experimental.

Since indeterminate errors cannot be eliminated experimentally, they must be evaluated mathematically. The general objective in this case is to obtain a measure of the precision of a series of divergent observations.

In order to illustrate some of the simple ways such a series of observations may be evaluated,[13] the percentages listed in Table 22.2 will be used.

[13] Elving and Mellon, *Anal. Chem.* **20**, 1140 (1948).

TABLE 22.2

EVALUATION OF ANALYTICAL DATA

Number	*Individual Percentage*	*Deviation from Average*	*Square of Individual Deviation* ($\times 10^4$)
1	9.52	+0.02	4
2	9.42	−0.08	64
3	9.53	+0.03	9
4	9.49	−0.01	1
5	9.58	+0.08	64
6	9.47	−0.03	9
7	9.51	+0.01	1
8	9.45	−0.05	25
9	9.55	+0.05	25
10	9.48	−0.02	4
TOTAL	95.00	0.38	206
AVERAGE, $\bar{X} = 9.50$		$D = 0.038$	$\sigma = \sqrt{\frac{206}{10^4}{n}} = 0.046$

The *arithmetical mean,* or average, $\bar{X}$, is obtained by dividing the sum ΣX_i, of all the individual observations X_i by their number n; that is,

$$\bar{X} = \frac{\Sigma X_i}{n}$$

For the data in Table 22.2, the sum 95.00, divided by the number 10, gives an average of 9.50, a value presumably more reliable than any individual value differing from it. If only the average is to be reported, the value should be simply 9.5. In accordance with the principles governing significant figures, as stated in Rule 4 (page 363), this value would then indicate a spread in the individual observations of more than 0.1 per cent, but nothing more.

Frequently it is desirable to know something more than is revealed by the simple average value. First of all, the number of observations averaged is likely to be of interest, since the value 9.5 might be the average of the two values 9.90 and 9.10 rather than the ten used in Table 22.2. To give an idea of the precision of the observations, the simplest way is to indicate the spread of the individual observations. For the ten values averaged in Table 22.2 the result can be written 9.50 ± 0.08 per cent, 0.08 being the maximum deviation from the average.

Since two values, 9.58 and 9.42, along with eight other values of 9.50 each, would give the same average as the ten values in the table, it may be desirable to indicate the distribution of the individual values around

the average. The simplest of these measures is the *average deviation D*, of the individual values from the mean value. This value is obtained, as shown in Table 22.2, by adding all the individual deviations, without regard to sign, and dividing by the number concerned. Stated in this way, the report would be 9.50 per cent, with an average deviation of ±0.038 per cent from the mean. In mathematical form, the average deviation may be stated

$$D = \frac{\sum_{i=1}^{n} | X_i - \bar{X} |}{n}$$

The *standard deviation* is considered a still more reliable estimation of precision. Since this calculation involves the squares of the values of the individual deviations, it serves to weight the values. As defined, the standard deviation σ is the square root of the sum of the squares of the individual deviations divided by the number of observations.[14] Or, in mathematical form

$$\sigma = \sqrt{\frac{\Sigma(X_i - \bar{X})^2}{n}}$$

With this measure of precision, our result becomes 9.50 per cent, with a standard deviation of ±0.046 per cent.

Limits of Uncertainty of an Observed Average

The statement that the average of the ten values in Table 22.2 is 9.50 ± 0.08 is the simplest, but also the least revealing, indication of the spread or range of the observed values. A more satisfactory basis is to use the mean, in connection with the standard deviation, to estimate the percentage of the total number of a group of experimental values which will lie in any stated interval about the average, or central, value. The latter alternative has been elaborated from a statistical basis by the American Society for Testing Materials. A brief adapation of the ASTM recommendations is given here.[15]

From this viewpoint, the problem is to present ± limits to indicate the uncertainty of the average of a number of observations obtained under the same essential conditions. An observed average $\bar{X}$ is subject to uncertainties that arise from operational fluctuations, and tends to vary

[14] For statistical reasons, some writers use $n - 1$ instead of n in calculating such data.

[15] American Society for Testing Materials, *ASTM Manual on Quality Control of Materials*, pages 41 to 51, 1951. Any ASTM material is reproduced (with slight changes) with permission.

from the objective average[16] more widely if the number n of observations is small.

Having a set of n observed values of a variable X (such as those in Table 22.2) the average of which is $\overline{X}$ one may wish to present the results as,

$$\text{Average } \overline{X} = 9.50 \pm ?\ \%$$

the $\pm$ limits being established from the quantitative data alone with the implication that the objective average $\overline{X}'$ of the universe[17] sampled lies within such limits. The question is how to compute such limits, and what meaning to attach to them.

Making certain assumptions regarding the statistical soundness of the data, the limits are given by the expression $\overline{X} \pm a\,\sigma$ where the value of the factor a is given in Table 22.3 for two probability values P and for selected values of n.

If the values of a given in Table 22.3 for $P = 0.95$ are used in a series of problems, then, in the long run, we may expect the ranges bounded by

TABLE 22.3

FACTORS FOR CALCULATING 95 PER CENT AND 99 PER CENT CONFIDENCE LIMITS FOR AVERAGES

(Limits within which $\overline{X}'$ may be expected to lie 95 times in 100, or 99 times in 100, in a series of problems, each involving a single group of n observations.)

	Confidence Limits $\overline{X} \pm a\,\sigma$	
Number n of Observations in Group	95% Confidence Limits ($P = 0.95$)	99% Confidence Limits ($P = 0.99$)
4	1.837	3.372
5	1.388	2.302
6	1.150	1.803
7	0.999	1.513
8	0.894	1.322
9	0.815	1.186
10	0.754	1.083
12	0.664	0.936
14	0.599	0.835
16	0.550	0.761
18	0.512	0.703
20	0.480	0.656
25	0.421	0.571

[16] The objective average $\overline{X}'$ is the value of $\overline{X}$ that would be approached as a statistical limit as more and more observations were obtained under the same essential conditions, and their cumulative averages computed.

[17] The "universe" comprises all there are of the entities being sampled.

the limits so computed to include 95 per cent of the time the objective averages $\bar{X}'$ of the universes sampled. If, in each instance, we were to assert that $\bar{X}'$ lies within the limits computed, we should expect to be correct 95 times in 100, and in error 5 times in 100; that is, the statement "$\bar{X}'$ lies within the range computed" has a probability of 0.95 of being correct. It should be emphasized that even in repeated sampling from the *same* universe, the range defined by the limits $\bar{X} \pm a\,\sigma$ will vary in width and position from sample to sample, particularly with small groups. It is this series of ranges fluctuating in size and position which will include, ideally, the objective average $\bar{X}'$ 95 times out of 100 for $P = 0.95$.

These limits are commonly referred to as *confidence limits*. For the two columns of Table 22.3, they are the 95 per cent and the 99 per cent confidence limits. The magnitude $P = 0.95$, for example, applies to the *series of instances*,[18] and is approached as a statistical limit as the number of instances in the series is increased indefinitely; hence, it signifies statistical probability.

Approximate values of a for other values of P may be read from the curves in Figure 22.3 for groups of $n = 25$ or less. The analyst will note at once that there is nothing here to apply to his common case of dealing with two or three observations. Even so, he should be at least aware of the general industrial developments in this direction, as exemplified by organizations such as the American Society for Testing Materials.

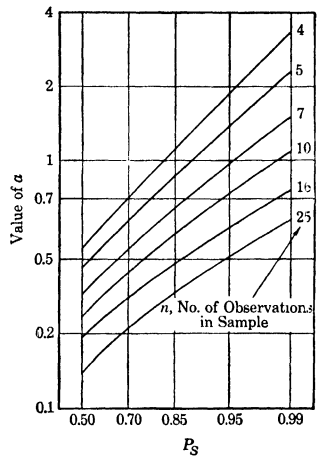


Figure 22.3

Nomograph for use in calculation of errors.

CONTROL CHARTS

Throughout industry a modified method of statistical evaluation of sets of data has been gaining increased recognition. Only recently have analysts begun to turn their attention to the possibilities inherent in this method of studying the variability of measuring numbers. The subject is too involved and extensive to discuss here, other than to mention

[18] This is a statistical term for the measurements or determinations being evaluated.

sources of further information and to give one example of application of the calculations. Reference should be made first, to the papers by Wernimont[19] and Mitchell,[20] and second, to the ASTM Manual on Quality Control of Materials.[21] In addition, the books by Brownlee[22] and Youden[23] go more into the mathematical background of the subject.

The general principle consists in the preparation of what are generally called *control charts*. A control chart may be described as a graphic presentation of test data in such a manner that the variability of all results is compared with the average variability within (arbitrary) small groups of test results. The chart is said to show evidence of control when there is no more variation throughout the entire set of results than corresponds, statistically, to the average variation within the (arbitrary) small groups.

In the paper by Mitchell the material quoted below is included as a recommended procedure for applying the quality control technic.

Collect Data

Plan the check sample test procedure, designed to reveal all the variations to which production samples are subjected. Include all analysts and equipment in the test. Study all varying conditions, such as time, lighting, and temperatures, and submit samples as planned under as many conditions as possible. Record the results, time, analyst, equipment, and other identifying and pertinent data. When 50 to 100 check results have been obtained, analyze the data as shown below. In many cases it will be desirable to analyze the data after 20 values have been obtained, depending upon the rate of analyzing the check samples and the necessity for rapid installation of a control system. If only three or four results are obtained per day, the control chart may be started at the end of a week; but it should be revised after about 100 values are obtained. If the data are obtained much more rapidly, as is often the case in production laboratories, 100 values are obtained in a short time.

Group the Data

The first step in determining the state of control of the data is to group the data into related sections. In most cases this grouping is most useful when made on a chronological basis, that is, the data are divided into groups in the order in which the samples were submitted for analyses. The size of

[19] *Ind. Eng. Chem., Anal.* Ed. **18**, 587 (1946).

[20] *Anal. Chem.* **19**, 961 (1947). The material quoted from this paper is reproduced with the permission of the author and of the editor of *Analytical Chemistry*.

[21] American Society for Testing Materials, "ASTM Manual on Quality Control of Materials," p. 55 (1951).

[22] Brownlee, *Industrial Experimentation*, Chemical, 1947.

[23] Youden, *Statistical Methods for Chemists*, Wiley, 1951.

each group is usually varied between two and ten values per group, although larger groups may be used for special purposes.

The exact size of the group will be varied according to production conditions and statistical considerations. If it is desired to check the precision and accuracy each day and only two values are obtained each day, a group size of two will be useful. If the test is in continual use and a check sample is

TABLE 22.4

DATA FOR CONTROL CHARTS

Analysis Number	X_1	X_2	X_3	ΣX	$\bar{X}$	R	$\sigma(\bar{X})$
1	10.06	10.09	10.05	30.20	10.07	0.04	0.021
2	9.91	10.05	10.04	30.00	10.00	0.14	0.078
3	10.08	10.07	10.15	30.30	10.10	0.08	0.044
4	10.07	10.05	10.03	30.15	10.05	0.04	0.020
5	9.99	10.18	10.09	30.26	10.09	0.19	0.095
6	10.06	10.08	10.04	30.18	10.06	0.04	0.020
7	10.10	10.08	10.00	30.18	10.06	0.10	0.053
8	10.11	10.02	10.21	30.34	10.11	0.19	0.095
9	10.06	9.87	10.02	29.95	9.98	0.19	0.100
10	10.03	10.06	10.19	30.28	10.09	0.16	0.085
11	10.05	10.08	10.06	30.19	10.06	0.03	0.016
12	10.05	10.08	9.96	30.09	10.03	0.12	0.062
13	9.94	10.04	10.05	30.03	10.01	0.11	0.061
14	10.04	10.07	10.09	30.20	10.07	0.05	0.025
15	10.06	10.01	10.10	30.17	10.06	0.09	0.045
16	9.85	10.02	10.03	29.90	9.97	0.18	0.101
17	10.07	10.13	10.01	30.21	10.07	0.12	0.060
18	10.09	10.03	10.07	30.19	10.06	0.06	0.031
19	10.06	10.10	10.04	30.20	10.07	0.06	0.031
20	9.86	9.89	10.00	29.75	9.92	0.14	0.074
21	10.02	10.11	10.07	30.20	10.07	0.09	0.045
22	10.07	10.01	10.08	30.16	10.05	0.07	0.038
23	10.05	10.20	10.03	30.28	10.09	0.17	0.093
24	10.06	10.17	10.23	30.46	10.15	0.17	0.087
25	9.99	9.92	10.04	29.95	9.98	0.12	0.060
				75)753.82		25)2.75	)1.440
	$n = 3$			$\bar{\bar{X}} = 10.05$		$\bar{R} = 0.11$	$\bar{\sigma} = 0.0576$

Limits of $\bar{X} = \bar{\bar{X}} \pm A_2\bar{R} = 10.05 \pm (1.023 \times 0.11) = \begin{vmatrix} 10.16 \\ 9.94 \end{vmatrix}$

Limits of $R = \begin{vmatrix} D_4\bar{R} \\ D_3\bar{R} \end{vmatrix} = \begin{vmatrix} 2.574\bar{R} \\ 0.0\bar{R} \end{vmatrix} = \begin{vmatrix} 2.574 \times 0.11 \\ 0 \times 0.11 \end{vmatrix} = \begin{vmatrix} 0.28 \\ 0.0 \end{vmatrix}$

Limits of $\sigma = \begin{vmatrix} B_4\bar{\sigma} \\ B_3\bar{\sigma} \end{vmatrix} = \begin{vmatrix} 2.692 \\ 0.0 \end{vmatrix} = \begin{vmatrix} 2.692 \times 0.0576 \\ 0 \times 0.0576 \end{vmatrix} = \begin{vmatrix} 0.015 \\ 0.0 \end{vmatrix}$

Average deviations $\begin{vmatrix} X_1 = 0.0495 \\ \bar{X} = 0.0376 \end{vmatrix}$ Standard deviations $\begin{vmatrix} X_1 = 0.0724 \\ \bar{X} = 0.0576 \end{vmatrix}$

ested once an hour, groups of four or eight will allow a check twice or once ach shift. In some cases it is desired to group the data according to analyst or equipment—for example, if there are ten testing stations in the plant and hree check results are run at each station per day, groups of three per station would be a logical system of grouping. In general, the smaller the size of he group, the more sensitive the chart becomes to individual variations. The arger the size of the group, the more sensitive the test becomes on slight changes of the average.

Calculate Limits for Groups

Calculate the averages of all groups, $\overline{X}$'s, and the total average, $\overline{\overline{X}}$. Calculate the standard deviations of all groups, σ's, and the average standard deviation $\bar{\sigma}$.

TABLE 22.5

FACTORS FOR COMPUTING CONTROL CHART LINES*

Number of Observations n *in Series*	*Chart for Averages*		*Chart for Standard Deviations*			*Chart for Ranges*		
	Factors for Control Limits		Factor for Central Line	Factors for Control Limits		Factor for Central Line	Factors for Control Limits	
	A_1	A_2	c_2	B_3	B_4	d_2	D_3	D_4
2	3.760	1.880	0.5642	0	3.267	1.128	0	3 267
3	2.394	1.023	0.7236	0	2.568	1.693	0	2.575
4	1.880	0.729	0.7979	0	2.266	2.266	0	2.282
5	1.596	0.577	0.8407	0	2.089	2 326	0	2.115
6	1.410	0.483	0.8686	0.030	1.970	2.534	0	2.004
7	1.277	0.419	0.8882	0.118	1.882	2.704	0.076	1.924
8	1.175	0.373	0.9027	0.185	1.815	2.847	0.136	1.864
9	1.094	0.337	0.9139	0.239	1.761	2.970	0.184	1.816
10	1.028	0.308	0.9227	0.284	1.716	3.078	0.223	1.777

Chart for	*Central line*	*Control limits*
Averages	$\overline{\overline{X}}$	$\overline{\overline{X}} \pm A_1\bar{\sigma}$
		$\overline{\overline{X}} \pm A_2\overline{R}$
Standard deviations	$\bar{\sigma}$	$B_3\bar{\sigma}$ and $B_4\bar{\sigma}$
Ranges	$\overline{R}$	$D_3\overline{R}$ and $D_4\overline{R}$

* This table is prepared from Table II, p. 63, *ASTM Manual on Quality Control of Materials*, 1951.

In many cases the range, R, is a good substitute for the standard deviation and involves less mathematics. However, when the groups are larger than four or five and the greatest efficiency is desired from a small amount of data, the standard deviation should be used.

Calculate [see Table 22.5 for symbols] the limits for the averages of the subgroups using the formula,

$$\text{Limits for } \overline{\overline{X}} = \overline{\overline{X}} \pm A_1 \bar{\sigma}$$

If the range is used in place of the standard deviation, use the formula

$$\text{Limits of } \overline{\overline{X}} = \overline{\overline{X}} \pm A_2 \overline{R}$$

Calculate limits of standard deviation from the formula,

$$\text{Limits for } \sigma = \begin{vmatrix} B_3 \bar{\sigma} \\ B_4 \bar{\sigma} \end{vmatrix}$$

If the range is used, calculate limits for the formula,

$$\text{Limits for } R = \begin{vmatrix} D_3 \overline{R} \\ D_4 \overline{R} \end{vmatrix}$$

Test for State of Control

Compare all averages and standard deviations or ranges with the control limits. This is most easily done in the form of a control chart in which all

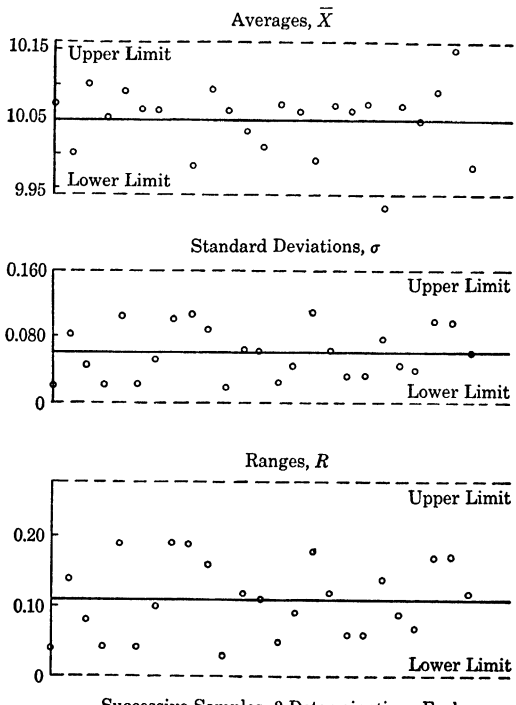


Figure 22.4

Control charts for averages, standard deviations of $\overline{X}$, and ranges of the data in Table 22.4. Each circle in the charts represents three determinations each for 25 successive samples.

group averages and standard deviations are plotted and the limits are shown by dotted lines. If any points are out of limits, this should be regarded as a sign of lack of control and the data on points out of control should be investigated. Often an error or abnormal conditions will be found. If causes for the points out of control are found, attempts should be made to prevent their affecting the test method in the future. If this can be done, these points out of control may be eliminated from the data and the study continued. Any points out of control limits must be regarded as a sign of lack of control and the method must be regarded as unreliable until causes of this abnormal variation are found.

If all points are within control limits, there is no evidence of lack of control. If 25 or more groups are all within control, we have reason to believe that the method is reliable.

In order to illustrate an application of this method, the data in Table 22.4 have been used, along with ASTM statistical constants in Table 22.5, prepared for computing 3-sigma (3σ) control limits. The raw data of Table 22.4 represents 25 analyses of a given sample, with three determinations, X_1, X_2, and X_3, per analysis.

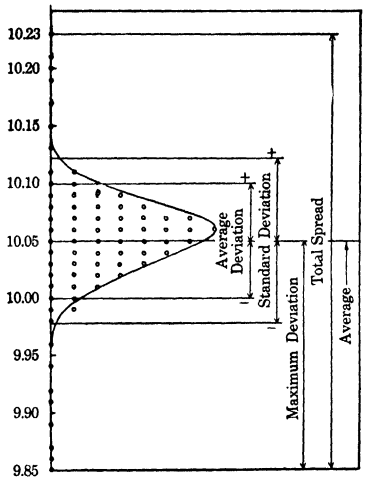


Figure 22.5

Data for the 75 individual values of Table 22.4.

Further details on the preparation of control charts, and of their meaning and use, may be found in the references cited.

In addition to the tabular form of Table 22.4 and the control-chart form of Figure 22.4, these data are presented in graphic form in Figure 22.5, in which each dot represents one of the individual values X_1 in the table. For these individual values the following items are shown: the grand average $\overline{\overline{X}}$, the limits for the average and the standard deviations, the total spread, and the limits of variation of the grand average $\overline{\overline{X}} + (3\sigma/0.724)$.[24]

[24] The value for $n = 3$.

CHAPTER 23

THE USE OF BALANCES[1]

This chapter is concerned with the use of analytical balances. The laboratory exercises deal with the determination of zero points, weighing, construction of a sensitivity curve, and checking weights.

In order to maintain a balance in working order and to secure reliable results with its use, the student should observe the following practical rules:

1. Keep the pans and balance clean.

2. Remove any dust from the pans with a camel's hair brush at the beginning of each laboratory period, before making the first weighing.

3. Note whether the balance seems to be operating properly before determining the initial zero point.

In releasing the beam support mechanism, turn the center control knob to the left slowly and carefully in order to prevent damage to the finely ground knife-edge bearings. Avoid sudden and forceful contact of the bearings.

4. Use counterpoised watch glasses only for weighing stable solids. Use stoppered weighing bottles for nonstable solids and all liquids.

5. Cool hot objects, or warm cold ones, to the temperature of the balance room before placing them in the balance case.

6. Always raise the beam rest into position before changing weights.

7. Close the case door before making the final adjustment of the rider (or chain), and again after the object and weights have been removed.

8. Handle the weights only with bone-tipped forceps. Return each piece to its proper position in the box when the weighing is completed. Leave the rider in the position occupied when the zero point was determined.

[1] See Chapter 3 for a general discussion of this subject and also for references on the care of balances.

9. Leave the balance with the beam and pan rests at their maximum height, and return the weight set to its assigned place.

10. Report to the instructor any loss of weights or difficulty with the balance.

NOTE TO INSTRUCTOR: The author devotes most of the first laboratory period to instruction in use of the balance. The students meet at the balance room and each is assigned his instrument. After a brief discussion of the significance of the balance and of weighing in analytical chemistry, the instructor directs the attention of the students to various details of adjustment of the level, swing of the pointer, the pan supports, the center of gravity, and the beam support. Following the instructor's lead, each student removes from his balance, in order, the right- and left-hand pans, and the right- and left-hand stirrups, taking time to examine each part for distinguishing marks corresponding to those on (or implied at) the ends of the beam. The plane agate bearings are examined. The beam is not removed from the case, but is lifted enough that the center bearings can be seen. Various items of construction are mentioned, particularly as they differ in various makes of balances.

When the balance is reassembled, the students are taken to the lecture room to see a movie prepared to illustrate the general operation of weighing. The film includes two methods of handling samples. One shows how to weigh the first sample used (barium chloride dihydrate) directly into the crucible in which the material is to be heated. The second shows the procedure for weighing an exact amount of sample, such as 0.5000 g for the iron determination, on a counterpoised glass, and for transferring the material to a beaker.

After the class returns to the balance room, weights are discussed briefly, including the method of adjustment used by the author so that corrections need not be applied. This discussion is followed by actual practice in weighing some object, including the recording of the value determined.

In the next class period the student is expected to be able to start his first analytical determinations and to make the necessary weighings.

Exercise 23.1. Determination of a Zero Point

Some point of reference for the swing of the pointer along the scale is necessary. Three common methods are used to determine this point, referred to as the *zero point,* on undamped balances and as the *rest point* on damped balances.

Before determining zero or rest points, the student should brush off the pans with a camel's hair brush and see that the balance is working smoothly. Then, with the pan rests lowered, the beam rest is released carefully so that the pointer will start to swing. Both beam and pan arrests drop on turning of the knob on single-control balances. Swings of the pointer of from 8 to 10 total scale divisions are usually satisfactory,

unless the method of short swings (described later) is used. In any case, a uniform practice should be adopted.

On balances having separate controls for the pan and beam rests, some operators prefer to release the beam rest first and then carefully lower the pan rests. This is the method followed in single-deflection weighing on undamped balances, described later.

In either case it is desirable, in starting the swings, to adopt some method of producing nearly uniform deflections. Usually this may be accomplished by learning to handle the control knobs in about the same way each time. If the balance has two riders, the one on the left may be used by placing it momentarily on the beam. Some foreign balances have a small rubber bulb with which to direct a puff of air on the bottom of one pan. Before closing the balance door, the operator may wave his hand enough to produce a slight current of air against one pan.

Single-Deflection Method

The single-deflection method is the most rapid for determining a point of reference, since only a half-swing of the pointer is used. The two variations in operating technic depend upon whether or not the balance is damped.

If the balance is *damped,* adjust the equilibrium-control nut to bring the rest point of the pointer 3 to 4 divisions off the center of the reference scale. Release the beam support, then the pan support. The pointer then swings to the rest point and remains there.

To weigh an object, add weights until the same rest point is obtained. Follow the same practice used to determine the initial rest point.

If the balance is *not damped,* adjust the pointer swing to go 3 to 6 divisions off center. Lower the beam arrest first, then the pan supports. Take the limit of the pointer swing as the zero point.

In general, the single-deflection method is used only on high quality, dual-control balances. Details of operation, including limitations for precise work, should be consulted.[2]

[2] Brinton, *J. Am. Chem. Soc.* 41, 1151 (1919); Kolthoff and Sandell, *Textbook of Quantitative Inorganic Analysis,* p. 218, Macmillan, 1952

Double-Deflection Method

The double-deflection method requires slightly more time than the previous method, but it is applicable to any undamped balance. It is also known as the method of short swings.[3]

To operate this technic, allow the first full swing to pass; then take one reading on each side of the center of the pointer scale.[4] Make a mental note of the difference between the two values. In weighing an object, add weights until the same difference between two swings is obtained. Keep the magnitude of the swings used in determination of the initial and final zero points approximately equal.

To use the alternative, short-swing technic, take one-half the difference between the values of a swing to one side and the next swing to the other side of the center scale mark. If deflections of 1 to 3 divisions are used, each swing decreases in amplitude very little.

Multiple-Deflection Method

The multiple-deflection method is sometimes known as the method of swings. Usually, three swings are taken on one side of the center of the scale and two on the other side, although more may be taken. There is mathematical justification for taking an odd number of swings in one direction and an even number in the other direction.[5]

To use this technic, start the pointer swinging and allow the first oscillation to pass. Then take five consecutive readings, three on one side and two on the other. Read the turning point on the scale for each swing. If the scale permits, note the reading to tenths of a division. Average each series, take the difference between the two values, and divide by two. The result is the calculated zero point, as shown by the following example for a balance having a scale graduated each way from the center.

Left	*Right*	
5.8	4.1	$5.6 - 4.0 = 1.6$
5.6	3.9	$\frac{1.6}{2} = 0.8$ (L)
5.4	2)8.0	
3)16.8	4.0	
5.6		

[3] Wells, *J. Am. Chem. Soc.* **42**, 411 (1920).
[4] Some operators prefer to count from zero at the left-hand end of the pointer scale.
[5] Fales, *Inorganic Quantitative Analysis*, p. 84, Century, 1925.

For these values, the zero point is 0.8 division to the left of the center of the scale.

This method is least rapid of the three described, but it is generally used for precision weighings. In weighing, an object would be counterbalanced with weights until the same calculated zero point is obtained.

Exercise 23.2. Weighing an Object

Two methods of weighing will be described. The first, the direct method, is used in all ordinary weighing in analytical work. The second, the substitution method, should be used in calibrating weights, or in any other work requiring provision for possible inequality of balance arms.

Direct Method

First, determine the zero (or rest) point by the technic to be used. Then raise both the beam and the pan supports.

By means of crucible tongs or other handling device, place the object to be weighed upon the left-hand pan. Lower the pan rests, if they are separately controlled, and fasten them down. If there is objectionable swinging of the pans, raise and lower the pan rests two or three times to stop the lateral motion. Then place on the right-hand pan, with the weight forceps, the weight judged to be nearest the mass of the object. Lower the beam support just enough to see which way the pointer moves, and then raise the support again. The weight will be either too heavy or too light. If it is too heavy, repeat the operation with a smaller piece or a combination of several of these. If it is too light, try one or more smaller pieces together with the first piece. Continue this "fit-and-try" procedure until the gram pieces selected are not quite enough to counterbalance the object.

When the fractional pieces are reached, continue the process of selection until the additional pieces on the pan are not quite sufficient to balance the object. Then close the balance door and locate the rider on the beam in the position which will give the same zero (or rest) point as that found for no load.

As an alternative technic in handling the fractional pieces, raise the pan supports and lower the beam support. Then control the balance by lowering the pan supports slightly to determine whether each fractional piece tried is too heavy or too light.

Adopt some consistent practice in placing the gram and the fractional pieces on the balance pan. Preferably, keep the gram pieces, the tenth-gram pieces, and the hundredth-gram pieces in separate groups. This grouping aids in noting the value of the weights used, when the final amount is on the balance.

In ascertaining the final mass value, read first the gram pieces and write the sum in the record book in the appropriate place. Then do the same for the tenth- and the hundredth-gram pieces to obtain the values for the first and the second decimal places, respectively. Finally, read the position of the rider and write down the third and fourth decimal places.

Next, carefully confirm the figures by observing the vacant places in the weight box, and recheck the rider position. As a final precaution, check the total by counting up the values of the pieces as they are returned to their places. *Checking the sum of the weights used is a precaution that the analyst cannot afford to neglect.* An error here can rarely be detected later.

If the fourth (or fourth and fifth) decimal place is to be determined by using the sensitivity curve, follow the technic described in Chapter 3.

If a chainomatic balance is used, follow the general sequence of operations described above until the rider weight is placed in the appropriate tenth-gram notch in the beam. To obtain the next three decimal places, lower or raise the "free" end of the chain until the zero-point reading is obtained. To do this, turn the knob at the right-hand end of the balance case base. Read the values of the second, third, and fourth decimal places on the dial by means of the vernier scale. If the balance is so equipped, read the numerals directly on the Veeder counter scale.

Substitution Method

To weigh an object by substitution, place it on the right-hand pan. Next, place some object on the left-hand pan of sufficient mass to serve as a counterpoise for the object being weighed. If necessary, place the rider somewhere along the beam in order to obtain a zero point at a suitable position on the pointer scale. Having achieved this objective, remove the object being weighed from the right-hand pan, and replace it with the combination of weights required to bring the swing of the pointer to the same zero point as at the beginning. Taking into account any shift found necessary for the rider, the value of the weights is the mass of the object being weighed.

If preferred, use the right-hand pan for the counterpoise, and reverse the order of balancing objects and weights against the counterpoise. In

such a case, take care in evaluating the significance of any shift in the position of the rider.

Exercise 23.3. Determination of the Sensitivity Curve

To determine the sensitivity curve for a given balance, dust off the pans and note the zero point with no load on the pans. Use the multiple-deflection method in this exercise if one of the other methods is to be used otherwise. Express the sensitivity as the number of scale divisions the zero point is displaced by a load of 1 mg.

Prepare the record book for a series of readings to be taken with zero, 10, 25, 50, and 100 g load on each pan. The following data illustrate such readings with no weights on the pans:

No Load

Rider at 0 mg		Rider at 1 mg	
Left	Right	Left	Right
3.2	5.1	8.2	+0.1
3.0	4.9	8.0	−0.1
2.8	2)10.0	7.8	2)0.0
3)9.0	5.0	3)24.0	0.0
3.0		8.0	

$$\frac{5.0 - 3.0}{2} = 1.0 \text{ (R)} \qquad \frac{8.0 - 0.0}{2} = 4.0 \text{ (L)}$$

$$4.0 + 1.0 = 5.0 = \text{sensitivity}$$

10 g LOAD
25 g LOAD
50 g LOAD
100 g LOAD

In carrying out this exercise, first determine the zero point with the selected load on each pan. To keep the reading at a suitable place on the scale, it may be necessary to place the rider somewhere along the beam. Next, move the rider 1 mg to the right on the beam and re-determine the zero point. As shown in the sample record, the shift in the zero point is the sensitivity.

Repeat the determination with loads of 10, 25, 50, and 100 (if available) g on the pans. Then construct a curve on co-ordinate paper similar to that shown in Figure 23.1. This figure includes a curve showing sensitivity expressed as milligrams per scale division.

Exercise 23.4. Checking Analytical Weights

Any careful determination of mass values by weighing necessitates the use of weights of known values. This information is obtainable only

by checking the set, unless a certificate is furnished from the National Bureau of Standards. The two most feasible methods of checking are included here.

Before use of either method, the pieces of a set should be carefully brushed and wiped with a chamois skin. If necessary, a very fine grade

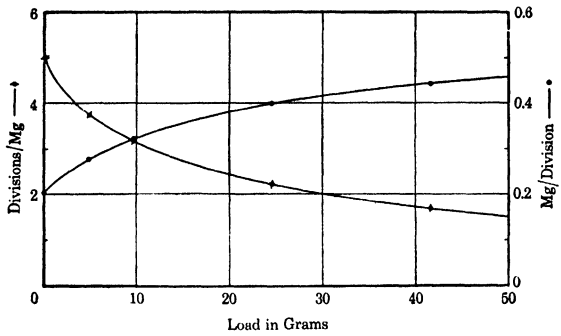


Figure 23.1

Sensitivity curve for balance.

of metal polish may be used lightly. After such handling, the pieces should stand for sufficient time to dissipate any electrical charge that may have been generated.

Adjustment to Specific Values

In following the method of adjustment to specific values, compare each weight in the set, piece by piece, with a N.B.S.-checked set. Use a high-grade analytical balance for the gram pieces and, if possible, an assay balance for the fractional pieces. Discard any of the latter pieces found to be more than 0.1 mg too light, unless they are gold or platinum and can be replated. If any pieces are too heavy, rub them lightly on fine emery cloth or on a fine file in order to remove the excess weight.

For any gram pieces needing adjustment, first remove the handle; then, if the piece is too heavy, empty out some of the filler in the base of the weight, or file lightly the base of the handle to make the piece too light. Then determine the deficiency for the piece made, or already, too light. Select the adjusting pieces required to meet the deficiency and place them in the base of the weight. Verify the corrected mass of the weight and then screw the handle back into the base.

Because the use of adjusted weights obviates the necessity of summing up and applying corrections for every weighing, the author prefers to use the method of individual correction for ordinary four-place weighing.

Determination of Individual Corrections

Careful calibration and application of the corrections is necessary for work of high quality, such as that requiring measurement to the fifth decimal place.

The details of the method, including several variations, are described in the reference papers cited on page 42. Also, the method may be found in several of the comprehensive texts listed in Chapter 32.

In using calibrated weights it is convenient to have the corrections arranged on a card in the balance case. For the pieces that are too light or too heavy, mark the corrections, respectively, negative and positive. For any given weighing, it is necessary to sum these corrections algebraically. Then this value is subtracted from (if minus) or added to (if plus) the observed sum of the nominal values of the weight pieces used.

Chains on chain balances should be checked if reliance on the values is critical in the fourth decimal place. A calibration curve may be determined by checking the chain reading at suitable intervals against appropriate standard weights. The curve may be plotted in the general form suggested in Figure 24.1 (page 396) for a buret.

CHAPTER 24

THE USE OF VOLUMETRIC WARE[1]

In checking volumetric ware to insure satisfactory performance in reasonably careful work, some items concern only the quality of the pieces and the convenience of their operation. Others concern the reliability of the data obtainable in measurements using the ware.

GENERAL OPERATIONS FOR CHECKING VOLUMETRIC WARE

Before starting the calibration of flasks, pipets, and burets, one should inspect each piece to determine whether it conforms to N.B.S. specifications, page 47. A record should be kept of the relevant data, following the form suggested by the instructor. A check mark ($\surd$) should be included to indicate each item meeting the specifications. Except for adjustment of drainage times of burets and pipets, and for cleanliness, little can be done about items that do not meet specifications. Tips of burets and pipets may be redrawn, if the time is too fast, or ground off, if too slow.

In addition to being leak-proof, the buret stopcock plug should turn easily and smoothly. To lubricate it, first wipe the contact surfaces clean and then apply enough lubricant[2] to form a thin film when the plug is turned around. Care should be taken to keep lubricant out of the hole through which the liquid must flow. In case lubricant does get into the tip, a buret probe of stiff wire may help temporarily if clogging occurs

[1] See Chapter 4 for a general discussion of this subject

[2] A satisfactory lubricant may be made by melting together 77.5 per cent white petrolatum and 15 per cent white paraffin (m p 53°) in a beaker suspended in an oil bath at 130° Add gradually 7 5 per cent of pale rubber crepe cut into shreds. Stir continuously for 6 hours. While the mixture is still just fluid, pour it in a thin stream on a cold, clean aluminum plate and work it over with a spatula until it is cool Keep in screw-cap salve containers [*Can. Chem Met* **9**, 137 (1925)].

Another recipe uses 10 parts of rubber (smoked sheet, or pale crepe), 18 parts of vaseline, and 1 part of paraffin (m p 30°) Commercial lubricants are also available

during use. It is best to remove petroleum-rubber products from the tip by means of a solvent such as carbon tetrachloride. For removal of silicone lubricants, 1,1-dichloroethane has been recommended.

Cleaning Interior Surfaces

A difficulty frequently encountered with volumetric ware is contamination of interior surfaces with material that prevents the formation of a uniform film on drainage. One possible contaminant is oily matter derived from steam, if the power house supply is used as a source of distilled water.

To clean the ware, several different solutions are recommended. Many analysts prefer one made by dissolving about 40 to 50 g of technical sodium dichromate in a liter of concentrated technical sulfuric acid. If necessary, the solution may be warmed to increase the rate of oxidation of organic matter. Often it suffices to rinse the surface to be cleaned. The solution should be returned to the stock bottle. More dichromate should be added when a green solution indicates reduction of the chromium to the tervalent state. If allowed to stand long in the buret stopcock, the solution attacks the lubricant and may produce a leak. The red deposit often seen is said to be $K_2(SO_4 \cdot CrO_3)$ when the potassium salt is used.

Other workers use solutions such as the following: a 15 per cent solution of trisodium phosphate heated to 70°; a solution of 9 parts of concentrated sulfuric acid to 1 part of concentrated nitric acid; a hot 1 to 2 per cent solution of a detergent; and a solution of 1 part of propylene glycol and 1 part of chloroform with a little powdered castile soap.

Whichever solution is used, the measuring piece must be thoroughly washed out with tap water, distilled water, and the liquid to be measured. It has been reported that such washing will not remove the last microquantities of chromium, if the dichromate solution is used.

Marking

Burets and pipets, and usually flasks, are purchased with graduation marks. New marks may be made on pipets or flasks by pasting a narrow strip of gummed paper with its upper edge marking the bottom of the correct position of the meniscus. For student use this paper may be covered with a coating of clear lacquer.

For permanent marking, cover the paper with a thin coating of paraffin and then carefully run a sharp knife-edge around the edge of the label. With a small brush put 2 drops of concentrated hydrofluoric acid on the

mark and rotate the piece 1 to 2 minutes to allow the acid to follow around the mark. Wash off the acid and remove the paraffin and label. *Take great care to avoid contact of the acid with the hands.* In case of contact the hands should be washed in water at once.

METHODS OF CALIBRATION

Volumetric ware is calibrated either by weighing the water delivered by or contained in a vessel, or by comparison of the piece with one previously checked. Each method is illustrated in the exercises.

Exercise 24.1. Calibration by Weighing the Water Contained or Delivered

Since the liter is defined in terms of a given mass of water, the basic method of calibration is to weigh the amount of water a given piece holds, if it is to be calibrated "to contain," or the amount delivered, if it is to be calibrated "to deliver." Occasionally, a pipet or flask is calibrated to use either way.

Flasks

Clean and dry thoroughly the flask to be calibrated. Counterpoise it upon the left-hand pan of a balance (*1*).[3] Then remove it and fill nearly to the mark with distilled water, boiled and cooled to room temperature. With a piece of filter paper remove drops adhering to the neck above the mark on the neck. From the fourth column in Table 4.7 (page 56), calculate the mass of water needed for the desired volume at the measured temperature, and put this value of weights on the right-hand pan. By means of a pipet add water carefully until the balance reaches its original zero point. Establish the mark as directed previously (*2*).

NOTES: (1) For flasks above 100-ml capacity a balance must be used capable of carrying heavier loads than those for which ordinary analytical instruments are designed.

(2) Rather than locate new marks some analysts prefer to use an established mark, even if it is not correct. The actual capacity of the flask is determined by weighing the water contained and a correction factor is calculated for use with the flask.

Pipets

Weigh a weighing bottle of suitable capacity, together with the stopper. Clean the pipet until it shows a uniform film on draining.

[3] Numerals in italics refer to explanatory notes at the end of the operating directions.

If the time of outflow is satisfactory (Table 4.4, page 50) fill the pipet with water of known temperature. Adjust the meniscus to the mark, touch the tip to a beaker to remove excess water, and allow the water to run into the weighing bottle. Touch the tip to the inside surface (below the ground glass), put on the stopper, and weigh the bottle. From the fourth column in Table 4.7 (page 56) calculate the amount of water that should be delivered by a correctly marked pipet at the working temperature. Compare the difference between this value and the amount delivered with the N.B.S. tolerance for this capacity pipet (Table 4.6, page 51). If the agreement is satisfactory, the pipet is ready for use.

If the deviation is not within the tolerance, the mark should be relocated. To do this, fasten a narrow strip of millimeter coordinate paper (5 to 6 cm long) lengthwise of the suction tube with the center of the scale near the graduation mark. Locate a definite mark at the top and bottom of the paper and weigh the water delivered between the two marks. Dividing the weight so obtained by the number of divisions gives the value per division. The error determined for the graduation mark divided by this weight of each division gives the number of divisions to change the mark. As a check, the water delivered from this new mark should be determined. Establish the position of the mark as directed for flasks.

Burets

First see that the buret is properly timed for flow (Table 4.5, page 51), lubricated, and cleaned. Fill it with water of known temperature. Weigh a 50-ml weighing bottle (*1*), adjust the meniscus to zero,[4] and run water into the weighing bottle until the meniscus is exactly at the 10.00-ml mark (*2*). After weighing the water, refill the buret and run out a 20.00-ml portion (*3*). Repeat the operation for 30.00, 40.00, and 50.00 ml (*4*). Note the temperature for each interval that is weighed. Record the data as directed by the instructor.

To calculate the true capacity at the several points, divide the weight

[4] In handling burets it is sometimes of advantage to use a meniscus reader. Such a device can be made cheaply from a clamp type of wooden clothes pin equipped with a spring so that the jaws may be clamped around the buret. Paint the wood black and paste a piece of white cardboard on the back. When the pin is placed with the upper edge a few millimeters below the meniscus, the bottom of the latter appears dark and is outlined sharply against the white background. A second simple aid in locating the position of the meniscus can be made by coloring the lower half of a 3 x 3 in. piece of thin cardboard or stiff paper with pencil or ink, and bending the upper half back slightly at the line between the colored and uncolored portions. In use, the card is placed behind the vessel with the line of demarcation several millimeters below the meniscus. A third device for meniscus reading is a collar-shaped section of thick black rubber tubing, cut open at one side and of such size as to clasp the tube firmly.

of water delivered by the weight of 1 ml at the given temperature (Table 4.7, column 4, page 56). Construct a calibration curve on coordinate paper by plotting volumes as ordinates and corrections (difference between the marked and the determined value) as abscissas (*5*). The form shown in Figure 24.1 is especially useful in that the N.B.S. tolerance values lie within the area of the isosceles triangle *ABC*.[5] Obviously, correction need be made only for curve values not coming inside the boundary of the triangle. By convention, negative values are located to the left of the zero vertical line and positive values to the right. Draw a smooth curve through the points (*6*). In using the buret later, apply the determined corrections unless they are within the N.B.S. tolerances. Negative corrections are to be subtracted from the buret reading and positive corrections are added.

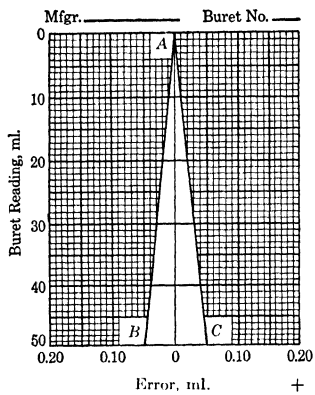


Figure 24.1

Form for buret calibration curve.

NOTES: (1) Weigh only to 3 decimal places, and avoid as far as possible touching the bottle.

(2) If the buret is unusually irregular, values should be determined at closer intervals.

(3) Most authors recommend running the intervals 0-10, 10-20, 20-30, 30-40, and 40-50. This method is shorter but follows less closely the practice of using a buret.

(4) Checking determinations should be made. They should agree within 0.03 g. Use the average of such values for the curve.

(5) For convenience in later use, the paper should preferably be lined closely enough so that each space will read 0.01 ml, since this value is the limit of readability on a 50-ml buret.

(6) Some individuals prefer to determine the average value of a milliliter for given intervals. Then, by a process of distributing the errors and rounding off to even values, a table showing the volume delivered at each milliliter on the buret may be constructed.

Exercise 24.2. Calibration by Comparison with Standard Pieces

If many pieces are to be checked, it is often preferable to use a previously calibrated piece. This is particularly true for flasks. Typical calibrating equipment is illustrated in Chapter 4, Figure 4.6.

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[5] See Mellon, *Quantitative Analysis Record Book,* Crowell, 1944.

Flasks

First determine that the standard bulb drains uniformly. Then fill it with water from the reservoir and adjust the meniscus to the mark to be used as zero. Touch the delivery tip to a beaker to remove any adhering drops. Bring the neck of the clean, dry flask under the tip and raise the flask until the graduation mark is about 1 cm below the tip. Open the stopcock and run the water out to the proper mark on the stem of the bulb. Note the position of the meniscus in the flask, and change the mark, if necessary, according to the procedure already described.

Pipets

An approximate, rapid method of checking pipets for gross errors consists in comparing the instrument with a flask of the same capacity. To do this, first paste a narrow strip of paper vertically across the mark on both the pipet and the flask. Then empty the pipet in the usual way into the dry, calibrated flask. The exact level of the water in the flask should be indicated with a fine pencil mark. If the location is not satisfactory, change it as follows:

If the meniscus is above the calibration mark of the flask, withdraw the excess water by means of a long-stem medicine dropper or glass tube and discard the liquid. Refill the pipet to the mark and allow sufficient water to run into the flask to bring the meniscus back to the pencil mark. Cover the delivery tip of the pipet with the finger and then make a mark on the paper at the new level on the pipet.

If the meniscus is too low, fill the pipet to the mark again and allow just enough water to run into the flask to bring its meniscus to the mark. Cover the delivery tip of the pipet with the finger and mark the point to which the meniscus has dropped in the stem. Locate the new mark above the graduation mark at a distance equal to the distance from the graduation mark to the pencil mark.

Burets

Connect the cleaned buret as directed to the bulb or calibrating pipet provided and fill the barrel of the buret with water. Open the buret stopcock. Turn the three-way stopcock on the calibrating pipet to allow the inside walls to become wet. Then drain the water out of the buret to zero and out of the pipet to the lower mark. Open the pipet stopcock and allow the water to rise until the meniscus just reaches the upper mark. Record the buret reading. Continue the operation until the calibration is completed, and then construct a curve as directed above

CHAPTER 25

NEUTRALIZATION METHODS[1]

Methods based upon neutralization reactions have long been divided into two groups, acidimetric and alkalimetric. These deal, respectively, with the determination of substances that are essentially basic or acidic in nature. For convenience each method will be discussed separately.

Acidimetry[2]

The methods of acidimetry include the preparation and use of solutions of strong acids, or of substances that give an acidic reaction, such as potassium hydrogen sulfate.

Solutions and Standards

Solutions of strong acids are used usually as titrants in determining substances which give an alkaline reaction in aqueous solution. Most often hydrochloric and sulfuric acids are employed, but occasionally some substance such as potassium hydrogen sulfate or potassium hydrogen phthalate serves. Except for potassium hydrogen phthalate, none of the compounds mentioned, as they are obtained commercially, are usable for primary standards.[3] Solutions of approximately the desired concentration must be prepared and their values carefully determined by some method of standardization.

[1] See Chapters 12 and 13 for a general discussion of this subject.

[2] Different types of titrimetric methods are named according to the kind of reaction or standard solution used. *Acidimetry* includes the use of standard acids.

[3] Specially prepared materials, sealed in glass ampoules, are available for dilution to prepare a variety of titrants of specific value. Examples of such products are the German "Fixanal," the British "Analar," and the American "Acculute" standards. Although carefully prepared systems, such as constant-boiling-point hydrochloric acid, potassium dichromate, and sodium chloride, should be reliable, the author is skeptical of substances for which analysts have not found satisfactory methods of stabilization.

It is possible to prepare a solution of hydrochloric acid of definite composition, known as constant-boiling-point acid. The method consists in boiling a solution having a specific gravity of about 1.10 until the boiling point becomes constant, and then collecting a portion of the distillate. The composition of this distillate depends upon the barometric pressure prevailing at the time of distillation. Reference to Table 25.1 (page 401) shows the amount to weigh out for 1 liter of a molar solution. A solution prepared in this way serves as a primary standard. In this respect, a solution so prepared is preferable to one made in any other way, as the method precludes the possibility of errors of standardization, except in weighing.

If acidic solutions are standardized, several types of methods are usually available, the precipitation-gravimetric and the titrimetric procedures being especially suitable. For the latter it is necessary to have some suitable primary standard that will react with the acid. The National Bureau of Standards has not provided such a substance, except as it is possible by careful heating to obtain sodium carbonate from standard sodium oxalate. Of the different substances that might be used, such as borax and similar salts, sodium carbonate is generally recommended. When prepared and used according to the procedures described, it is quite satisfactory.

Applications

The substances that can be determined acidimetrically, by means of solutions of strong acids as titrants, include hydroxides having dissociation constants greater than 10^{-8}, e.g., sodium and ammonium hydroxides, and salts of strong bases and weak acids, e.g., sodium carbonate. In general, this list might be extended to include any substance that will react quantitatively with an acid and for which a suitable means for determining the equivalence point is available.

Some substances, such as calcium carbonate, are too insoluble for a satisfactory direct titration. In this case, resort may be made to the common practice of back titration. An excess of a standard acid is added to dissolve the sample. The amount not used in the reaction is determined by titrating back with a standard alkaline solution.

In the discussion of indicators and of means for determining equivalence points, in Chapter 13 it was pointed out that bases having very small ionization constants cannot be titrated satisfactorily in aqueous solution. Reference was made to the possibility of using nonaqueous solvents for titrating some substances of this kind.

Exercise 25.1. Preparation of Pure Sodium Carbonate

Since commercially obtainable sodium carbonate does not ordinarily have the requisite degree of purity to serve as a primary standard, it must be prepared. Waldbauer, McCann, and Tuleen[4] proposed washing a reagent-quality sodium carbonate with ethanol to dissolve out possible impurities and then weighing the dried product directly. A more common practice is to heat sodium hydrogen carbonate, which can be obtained sufficiently pure, to a point where it decomposes according to the equation

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O\uparrow + CO_2\uparrow$$

If tests[5] show that chlorides, sulfates, or potassium are present in appreciable amounts, the hydrogen carbonate salt should be recrystallized by evaporating a saturated solution at a temperature under 40° until crystallization begins.[6] Then the solution is cooled and filtered through a fritted glass funnel, and the crystals air-dried.

Procedure

Place the purchased or purified sodium hydrogen carbonate in a dish, preferably of platinum, and set it in an electric furnace, the temperature of which can be regulated between 260 and 290° (*1*). Allow the material to remain at this temperature long enough to volatilize all the water and carbon dioxide (*2*). Cool the carbonate in a desiccator and store the material in a tightly stoppered container (*3*).

If a suitable furnace is not available, students may make their standards individually by placing about 5 g of the salt in a weighing bottle and heating the uncovered bottle in a sand bath. The bottle should be three-fourths immersed and the temperature determined by means of a thermometer close by in the sand. At the end of an hour, cool the bottle to room temperature in a desiccator, replace the bottle cover, and weigh. Repeat the process until constancy of weight is attained. This indicates complete conversion to the carbonate.

NOTES: (1) Insufficient heating will not completely decompose the hydrogen carbonate. Excessive temperatures may produce some oxide, the product then being both hygroscopic and of uncertain composition.

(2) Each batch of stock material should be tested against a previously standardized acid to insure complete conversion. Experience will indicate a safe length of time to

[4] *Ind. Eng. Chem., Anal. Ed.*, **6**, 336 (1934).

[5] Wichers *et al., Reagent Chemicals: American Chemical Society Specifications, 1950, Am. Chem. Soc.*, 1951 (see page 561).

[6] Biltz, Hall, and Blanchard, *Laboratory Methods of Inorganic Chemistry*, p. 134, Wiley, 1909.

heat the amounts used. Heating for 5 hrs. suffices for the contents of a 200-ml platinum dish.

(3) This and other solid primary standards may be conveniently dispensed for student use by putting a sufficient amount in 10-ml vials which are then kept ready at the laboratory.

Exercise 25.2. Preparation of Constant-Boiling-Point Hydrochloric Acid [7]

During distillation of aqueous solutions of hydrochloric acid, dilute solutions lose water more rapidly than acid, and concentrated solutions lose acid more rapidly than water. Under similar conditions, they ultimately reach the same composition, as indicated by the attainment of a constant boiling point. The exact composition depends upon the barometric pressure at the time of distillation, as shown in Table 25.1.

Procedure

To 250 ml of concentrated acid in a 500-ml side-arm distilling flask add 200 ml of distilled water (*1*). Insert a thermometer in the neck of the flask, with the bulb opposite the delivery tube, and connect the latter to a suitable glass condenser.

Heat the flask sufficiently to distill the liquid at a rate of 3 to 4 ml per minute. If the thermometer indicates the attainment of a constant boiling point (*2*) after one-half to two-thirds of the solution has distilled, begin to collect the distillate in a clean, dry, glass container, which can be closed with a glass stopper. Note the corrected barometric pressure during the period of distillation (*3*). Discontinue the distillation when

TABLE 25.1

ANALYTICAL DATA FOR CONSTANT-BOILING-POINT HYDROCHLORIC ACID

Barometric Pressure	*Per Cent HCl by Weight*	*Grams of Solution for 1 Mole HCl**
770	20.215	180.40
760	20.239	180.19
750	20.263	179.97
740	20.286	179.76
730	20.311	179.55

* Air weight.

[7] Foulk and Hollingsworth, *J. Am. Chem. Soc.* **45**, 1223 (1923). See also Bonner and Titus, *J. Am. Chem. Soc.*, **52**, 633 (1930), and Titus and Smith, *J. Am. Chem. Soc.*, **63**, 3266 (1941).

50 to 60 ml of solution remain in the distillation flask. Stopper the container.

The data in Table 25.1 show the amount of constant-boiling-point solution to take in order to obtain 1 mole of hydrogen chloride.

NOTES: (1) Time is saved by starting with a solution of sp. gr. 1.10, which is near the constant-boiling-point composition.

(2) At a pressure of 750 mm, the temperature is near 109° (uncorrected) when the constant boiling point is reached.

(3) Only the barometric pressure prevailing at the time of distillation is of significance. The observed pressure should be corrected for altitude and temperature.

Exercise 25.3. Preparation of a Standard Solution of Hydrochloric Acid

To make a standard solution of hydrochloric acid one may use either the constant-boiling-point material already described or commercial concentrated acid. The former may be handled directly, as any primary standard is used. With the latter it is necessary to prepare the solution of the approximate concentration desired, and then to determine the actual concentration, by means of one of the methods outlined in Chapter 12. The only guide to the composition of the commercial acid is the statement on the label regarding limits for the specific gravity and the percentage composition.[8] In making calculations the lower values may be used.

If a standard solution of an alkali is available, the solution of acid may be standardized by titration with the standard alkaline solution, as subsequently described for the standardization of sodium hydroxide solution *versus* a standard acid solution. Such a procedure may yield less accurate results than a direct titration of a primary standard by the acid solution, since the errors, if any, in the standardization of the alkaline solution are superimposed on those involved in the titration of the acid with the base.

An acid solution can, in many cases, be standardized by a gravimetric measurement of the anion of the acid. In the case of hydrochloric acid solutions, the chloride ion can be precipitated and weighed as silver chloride; for sulfuric acid solutions, barium sulfate may be separated and weighed.

The general method of preparing standard solutions of other acids, such as sulfuric, is substantially the same as that described below for the use of concentrated hydrochloric acid. As previously mentioned, solutions of hydrochloric or sulfuric acid serve for most of the titrations encountered by the analyst.

[8] See a chemical handbook for a specific gravity-composition table.

Use of Constant-Boiling-Point Acid

From Table 25.1 determine, by interpolation if necessary, the amount of constant-boiling-point acid required for the solution to be prepared, calculating only to the nearest centigram. This will be about 18 g for a liter of 0.1 *M* solution. The exact amount calculated may be weighed into a clean, dry weighing bottle, the weight of which has been previously determined. This process involves the customary difficulties encountered in taking exact amounts of a liquid (*1*). Wash the weighed acid into a volumetric flask, dilute to the graduation mark, and mix. Unless an exact concentration is desired, it is easier to weigh to the required number of decimal places an approximate amount and then calculate the concentration.

NOTE: (1) To make the weighing, counterpoise the bottle, and then put the calculated amount of weights on the right-hand pan. Carefully add acid to the weighing bottle on the left-hand pan from a pipet, until about the desired amount is transferred. Use care to avoid getting any acid on the pan. Final adjustment may be made with a piece of glass tubing drawn out to a tip 10 to 15 cm long.

Use of Laboratory Acid

Two procedures are given for preparing the solution, one for obtaining an approximate but definitely known concentration and one for an exact concentration. The former is given first.

Assuming that a solution exactly 0.2000 *M* is to be prepared (*1*), calculate the number of milliliters of concentrated acid to take for 2300 ml (*2*) of a solution, using the values for percentage composition and specific gravity found on the label, and allowing 2 per cent excess to insure a solution slightly too concentrated. Measure the acid in a graduated cylinder, transfer it to a clean 2500-ml acid bottle (*2*), add about 2250 ml of distilled water, and mix *thoroughly*.

Of the different methods available for standardizing the acid, the two given here are based on a comparison with sodium carbonate.

Method I. Procure or prepare standard sodium carbonate for the standardization. Calculate the amount required to react with 35 ml of 0.2 *M* acid (*3*). Weigh on a counterpoised watch glass three separate dried portions of about this amount, noting in each case the exact amount to four decimal places (*4*).

Brush each carefully into a 250-ml conical flask, using a short, wide-stem funnel to facilitate the transfer. Wash into the flask any material adhering to the funnel, dissolve in 40 to 50 ml of water, and add 2 drops of methyl orange, or modified methyl orange, indicator solution (*5*).

Clean a smoothly lubricated buret until it drains uniformly, and rinse it

out thoroughly by using finally two 10-ml portions of the solution to be standardized. Then fill it with this solution (*6*) and adjust the meniscus carefully to zero. Now allow the acid to run into the carbonate solution, swirling the solution in the flask with the right hand and controlling the buret with the left by encircling the barrel of the buret with the thumb and forefinger so that the stopcock is always pressed gently inward in turning. Observe the flashes of color where the acid meets the surface of the carbonate solution. As the end point is approached, the original color is less and less persistent, and the titrant should be added more slowly. At the end point with methyl orange, the solution is just definitely pink, or, with modified methyl orange, the green just disappears to leave an almost colorless, or faintly purple solution.

Titrate the other portions and calculate the normality or molarity for each titration. When two consecutive values are obtained which agree to within 2 parts per 1000, calculate the average value (*7*). The solution may be employed without adjustment, using the average normality to calculate titers (equivalencies) for the constituents to be titrated with it.

If the solution is to be adjusted to exactly 0.2000 *M*, calculate the ml of water per liter to add (*8*). If the amount is large enough to bring in the question of changes of volume on mixing, somewhat less than the calculated amount should be added, the concentration redetermined, and the ml/liter of water again calculated. Preferably, the diluted solution should be checked again (*9*). When the required information has been put on the label (*10*), leave the solution with a laboratory assistant for verification (*11*), if so directed by the instructor.

Method II. Calculate the weight of sodium carbonate for 250 ml of a 0.2000 *N* solution. Weigh the exact amount on a watch glass, transfer the salt into a short-stem funnel in the neck of a 250-ml volumetric flask, dissolve in water, dilute the solution to the graduation mark, and mix well (*12*). With a clean 25-ml pipet, which has been rinsed with a little of this solution, transfer three separate 25-ml portions to 250-ml conical flasks, add about 25 ml of water, and titrate as in Method I. Calculate the required concentration values.

NOTES: (1) The symbol 0 2 *M*, and any others similarly used, are intended to imply that the value is defined to four signficant figures, as 0.2000 *M*.

(2) Preparation of 2300 ml of solution leaves room for mixing.

(3) Complete neutralization of the sodium carbonate is assumed, using methyl orange as the indicator.

(4) To weigh "by difference," determine the weight of a weighing bottle containing the carbonate, empty into a titration flask about the desired amount, and reweigh the bottle. Handle the bottle as little as possible and allow time for electrical charges to become dissipated if the container has been wiped with a cloth.

(5) The hue will be yellow or green, depending upon whether the ordinary or modified solution is used.

(6) A small, short-stem funnel or thistle tube is convenient to use in the end of a buret when pouring in solutions from a large container. The funnel should be removed before adjusting the solution to zero.

(7) The buret reading used in making calculations should take into account the correction indicated by the calibration curve, and also the temperature correction, if it is applied.

(8) The method for calculating the water per liter to add is given in Chapter 33, under dilution problems.

(9) The concentration may be adjusted by diluting the calculated number of milliliters to 1 liter (see Chapter 12).

(10) The label should contain at least the date of preparation, the name or formula of the acid, the average normality or molarity, the required titers, and the owner's name.

(11) It is desirable to have the first standard solution checked by an instructor by titration against another standard solution.

(12) Sodium carbonate solutions should not be kept longer than one week.

Exercise 25.4. Determination of the Alkalinity of Soda Ash

"Soda ash" is a term applied to the commercial grade of sodium carbonate. For various industrial purposes the most important characteristic of the material is its neutralizing capacity. This may be measured by titration with an acid. Since the neutralizing capacity is attributable to sodium carbonate more than to any other constituent, the results are currently reported in terms of this compound or of sodium oxide. Such a titration measures the total acid-consuming constituents of the sample, and does not specifically indicate that some of the acid may be used in reacting with such constituents as potassium carbonate or sodium hydrogen carbonate, if they are present in the sample.

The Sample

Selection and preparation. If the sample must be selected from a commercial lot, follow the suggestions given in Chapter 2 for securing representative portions and mixing them. Some lack of fineness may have to be tolerated rather than risk too much exposure to the air with resultant absorption of water. Put the sample in a weighing bottle.

Measurement. Weigh (*1*) the weighing bottle containing the dried sample (*2*), empty about 3 g (*3*) into a dry, short-stem funnel placed in the neck of a 250-ml volumetric flask and reweigh the weighing bottle (*4*).

Treatment. Wash into the flask any material adhering to the funnel, fill the flask three-fourths full of water, dissolve the sample, dilute to the mark, and mix thoroughly.

The Desired Constituent

Measurement. With a clean pipet (*5*) transfer a 25-ml portion to each of several 250-ml conical flasks. Add one to two drops of plain or modified methyl orange and titrate with the standard acid (*6*). Repeat the titration with other portions until two consecutive results are obtained which check within the limits prescribed (*7*). Calculate the percentage of sodium carbonate and of sodium oxide (*8*) for each portion, and then determine the average percentages, keeping in mind the rules for significant figures.

NOTES: (1) Before recording any data, consult the bulletin board for an approved form for the report.

(2) If synthetic samples are dispensed, they may be weighed directly on a watch glass.

(3) Weighing a large sample and using aliquot portions of the solution serve to reduce the possibility of errors arising from inadequate mixing and preparation of the sample.

(4) How much sample should be taken if an aliquot of one-fourth is to require at least 25 ml of the standard acid, assuming the material is pure sodium carbonate?

(5) If the pipet is not clean and dry, it should be cleaned and finally rinsed with some of the solution that is to be measured.

(6) If the first titration requires less than 10 ml of acid, increase the size of the aliquots in subsequent titrations.

(7) For beginners, 5 parts/1000 is reasonable.

(8) Some industrial uses of soda ash are based upon the content of the oxide, Na_2O.

Exercise 25.5. Determination of a Mixture of Hydroxide and Carbonate[9]

When a material such as caustic soda is exposed to the atmosphere, the sodium hydroxide absorbs both water and carbon dioxide. If such a substance is to be examined for its neutralizing capacity, a single titration with an acid in the presence of methyl orange suffices, as in the preceding exercise. If information is desired concerning the extent of the contamination mentioned, advantage may be taken of an interesting use of two indicators.

Reference to Figures 13.3 and 13.4 (pages 205 and 207) will indicate what may be expected to happen when a solution containing sodium hydroxide and sodium carbonate is titrated. The curves show that, by the time a *p*H value of 8.3 is reached, the hydroxide will be neutralized and the carbonate will be transformed to the hydrogen carbonate. If phenolphthalein is used as the indicator, it will become colorless at this

[9] See Benedetti-Pichler *et al., Ind. Eng. Chem., Anal. Ed.* 11, 327 (1939).

stage. On addition of methyl orange, the titration may be continued to measure the hydrogen carbonate.

In the first titration, for which A ml of titrant is required, all the hydroxide is neutralized and the carbonate is one-half neutralized, according to the equations

$$NaOH + HCl \rightarrow NaCl + H_2O$$
$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$$

In the second titration, for which B ml of titrant is required, the completion of the neutralization of the carbonate occurs, as shown by the equation

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2\uparrow$$

In the calculation, A minus B = volume of solution required for NaOH, and 2 B = volume of solution required for Na_2CO_3.

The method is equally applicable to commercial potassium hydroxide (caustic potash), and to mixed carbonate and hydrogen carbonates of potassium.

A more complicated example of the use of two indicators has been discussed by Gerber and Miles.[10] The determination involves analysis of a mixture of ortho-, pyro-, and metaphosphoric acids (H_3PO_4, $H_4P_2O_7$, and HPO_3).

The Sample

Selection and preparation. Select a sample as representative as possible and store it in a stoppered container. The material may be mixed rapidly, but extensive grinding will entail change of composition by absorption of water and carbon dioxide.

Measurement. From a stoppered weighing bottle weigh by difference an amount of sample such that, when it is dissolved to make 1000 ml of solution, the titration of a 50-ml portion will require 30 to 40 ml of acid for the first titration (*1*).

Treatment. Transfer the sample to a liter flask, dissolve in recently boiled water, cool to room temperature, dilute the solution to the mark, and mix (*2*).

The Desired Constituent

Measurement. With a pipet transfer 50 ml of the solution to a conical flask and add one to two drops of phenolphthalein indicator solution.

[10] *Ind. Eng. Chem., Anal. Ed.*, 10, 519 (1938).

Cool to near zero by immersing the lower part of the flask in a casserole or dish containing ice water (*3*), and titrate *slowly,* with constant stirring, to a colorless solution. Record the volume of acid used. Remove the cooling vessel, add one to two drops of methyl orange indicator solution to the sample, and continue the titration until the color change indicates that the solution is just acidic (*4*). From the two volumes of acid used, calculate the percentage of sodium hydroxide, sodium carbonate (*5*), and inert material.

NOTES: (1) For the calculation, assume the sample is sodium hydroxide.

(2) Distilled water prepared from "hard" sources contains considerable carbon dioxide that will react with the sample. (How?)

(3) Slow titration at a low temperature prevents, insofar as possible, the loss of carbon dioxide. What reaction would liberate it, and what would be the effect on the results? Since the reaction is difficult to control when carbonate is present, the method should be applied only when the carbonate is present as an impurity.

(4) Why may the second titration be made more rapidly without detracting from the reliability of the results?

(5) This analysis illustrates the difficulty encountered when one constituent is present in large amount and another in small amount. A sample large enough to make the reading errors negligible for the lesser constituent would require inconveniently large amounts of titrant for the more abundant constituent.

Alkalimetry

The methods of alkalimetry include the preparation and use of standard solutions of strong bases, or of substances that give an alkaline reaction, such as sodium carbonate.

Solutions and Standards

The compounds generally used for preparing standard solutions include sodium, potassium and barium hydroxides, and sodium and potassium carbonate. The carbonates can be secured in a form suitable for preparation by direct weighing, but the hydroxides must be standardized. At one time benzoic acid, C_6H_5COOH (N.B.S. No. 39), was recommended as a primary standard for checking alkaline solutions. The small solubility of the compound in water is a handicap. Potassium hydrogen phthalate, $KHC_8H_4O_4$ (N.B.S. No. 84), is now recommended because of its desirable properties, including solubility. Constant-boiling-point hydrochloric acid is a serviceable standard, if carefully prepared.

Two other substances used for standardizing alkalies are sulfamic acid HSO_3NH_2, and potassium hydrogen iodate $KH(IO_3)_2$. Each reacts as a strong monofunctional acid. The iodate also serves in redoximetry.

All of the alkaline solutions mentioned are subject to more or less change in concentration when kept in ordinary glass containers, as a result of their action on the glass. Since they seem to become more alkaline, the action presumably involves dissolution of sodium silicate from the glass. The action seems to be less in Pyrex than in flint glass. Corning No. 728 glass is nearly boron-free and is recommended where resistance to alkaline solutions is important.

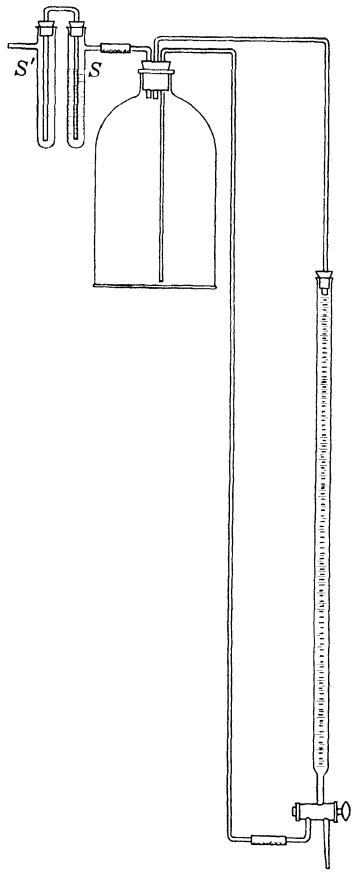


Figure 25.1

Arrangement for excluding carbon dioxide from a standard base.

To protect glass bottles against alkaline attack, the analyst may coat the inside of the bottle with paraffin. The vessel should be thoroughly dried and warmed to 70 to 80° over a hot plate or steam bath. The melted paraffin is put inside and the vessel rotated in such a way that, as the temperature drops, a uniform coating will be obtained. If the solution has to be kept long, this procedure may not be particularly satisfactory, since frequently, if the weather is warm, the paraffin does not stick well to the glass. For such solutions vessels of nickel [10] or stainless steel (18-8)[11] have been recommended.

Absorption of carbon dioxide from the atmosphere is another reaction which may affect the concentration of alkaline solutions. In the case of barium hydroxide, the concentration is reduced through the precipitation of barium carbonate. When the carbonate formed is soluble, the effect is also an apparent reduction in concentration if the solution is used with indicators of the higher *p*H ranges, such as phenolphthalein.

A satisfactory means for preventing contamination with carbon dioxide during use of the solution is the arrangement of storage bottle and buret

[10] Righellato, *Analyst*, **59**, 104 (1934).
[11] Flanders, *Ind. Eng. Chem., News Ed.*, **18**, 1134 (1940).

illustrated in Figure 25.1. The guard tube S is half-filled with a 15 per cent solution of sodium hydroxide. The second tube S' serves to catch the protective solution if a rise in temperature forces it back from S.

If the barium ion does not interfere in the titrations for which the solution is to be used, one may add enough barium hydroxide or some soluble barium salt to precipitate the dissolved carbonate as barium carbonate. After this precipitate has settled out, the clear solution may be carefully transferred into another bottle containing carbon-dioxide-free air.

Applications

The titrimetric application of standard solutions of hydroxides is confined to systems that will react with the titrant and for which a suitable end point can be found. The list includes acids the ionization constants of which are sufficiently large, together with a number of other substances that may be determined by adding an excess of a standard acid and back titrating with hydroxide.

Exercise 25.6. Preparation of a Standard Solution of Sodium Hydroxide

It has been nentioned that a solution of sodium hydroxide will absorb carbon dioxide from the air. Even the best grades of this solid contain more or less carbonate. In many cases standard solutions made from this material are quite satisfactory, but for some purposes solutions free from carbon dioxide are required. Since alkaline solutions must be restandardized if kept more than a few days, it is not worth while to adjust their concentration to an exact value.

Unless some special requirement is to be met, sodium hydroxide is used for preparing solutions. Potassium hydroxide is specified for work with saponifiable oils because of the greater solubility of the potassium soaps formed. Barium hydroxide is used in determinations such as the Pettenkofer method for carbon dioxide in air and the titrimetric method for carbon in steel. In both these cases, the carbon dioxide reacting produces a precipitate of an equivalent amount of barium carbonate, and the excess hydroxide is back titrated with an acid.

Procedure I: Sodium Hydroxide Not Free of Carbonate

Use reagent-quality sodium hydroxide pellets or sticks (*1*). Weigh the approximate amount calculated for 2 liters of 0.2 M solution (*2*). Transfer to a 500-ml beaker and add 300 ml of distilled water to dissolve the hydroxide. Pour the solution into a 2.5-liter bottle and add about 1700 ml more of distilled water. Shake the bottle until the solution is

thoroughly mixed (*3*). With a pipet, transfer 25-ml portions to conical flasks (*4*), dilute with a little water, add one to two drops of methyl orange indicator solution, and titrate with the previously standardized acid (*5*). Duplicate determinations should check within the limits prescribed (usually a few parts per thousand).

Repeat the standardization with methyl red and phenolphthalein as indicators. In the case of phenolphthalein, perform the titration in both directions, i.e., titrate acid with hydroxide (*6*) and hydroxide with acid (*7*). Calculate the normality for each indicator, and the respective titers for any constituents to be determined with the hydroxide solution (*8, 9*).

NOTES: (1) If the carbonate covering the surface of commercial sodium hydroxide is objectionable, most of the effect may be avoided by preparing the solution by diluting with distilled water an appropriate volume of a clear, saturated aqueous solution of sodium hydroxide, in which the carbonate is relatively insoluble.

(2) For most ordinary work a solution between 0.1 and 0.2 *M* is satisfactory.

(3) If the solution is warm, why must it cool to room temperature before standardization?

(4) The standard acid may be titrated with the hydroxide. Do not leave a solution of hydroxide standing long in a glass stopcock buret since ground glass surfaces are attacked rapidly and the stopcock "freezes."

(5) A primary standard, such as constant-boiling-point hydrochloric acid or potassium hydrogen phthalate, may be used for the standardization.

(6) A fading end-point is encountered in titrating acid with hydroxide in the presence of phenolphthalein, inasmuch as the absorption of carbon dioxide from the air reverses the reaction. Bubbling carbon dioxide-free air through the acid being titrated avoids the difficulty. Usually analysts shake the solution with gentle swirling only, and take as the end-point the first pink persisting throughout the solution for 30 sec.

(7) The difference in the values obtained for methyl orange and phenolphthalein indicates why the solution must not be standardized with one indicator and then used with the other without applying the respective normality.

(8) It is especially important to record the date of standardization of a nonpermanent solution.

(9) If carbon dioxide-free water is needed in quantities, it may be prepared conveniently by bubbling carbon dioxide-free air through a carboy of water for several hours.

It is instructive to determine carefully the ratio, acid/base or base/acid, using one of the three indicators mentioned and titrating in both directions.

Procedure II: Sodium Hydroxide Free of Carbonate

Proceed as in Procedure I in calculating the amount of sodium hydroxide needed. Transfer the weighed amount to a 500-ml beaker and dis-

solve in about 300 ml of distilled water. To the warm solution add slowly 25 ml of 0.25 *M* barium chloride solution. After the barium carbonate settles, decant the clear solution into a liter flask and dilute to volume with carbon dioxide-free water [Note (9), Procedure I]. After any further precipitate settles, siphon or filter the clear solution into a bottle. An arrangement similar to that shown in Figure 25.1 should be used if the analyst desires to keep out as much carbon dioxide as possible.

The analyst may largely eliminate the carbonate present by using a saturated solution of sodium hydroxide as a stock material. The carbonate is relatively insoluble under these conditions and settles out, so that the clear liquid may be siphoned off. [Note (1), Procedure I].

Either of the two methods described below may be used to standardize the solution.

1. Standard hydrochloric acid. If standard hydrochloric acid is used, the solution is standardized according to Procedure I, given above. With phenolphthalein as the indicator, the best results are obtained when the acid is titrated with the hydroxide. Bubbling a slow stream of carbon dioxide-free air through the solution being titrated gives excellent end points with phenolphthalein.

2. Potassium hydrogen phthalate. The following directions are recommended for the use of potassium hydrogen phthalate, $KHC_8H_4O_4$ (N.B.S. Standard No. 84).

Lightly crush a few grams of the salt to a fineness of approximately 100 mesh and dry for 1 to 2 hrs. at 120°. Place in a small glass-stoppered container and cool in a desiccator. Accurately weigh about 1 g of the dried salt and transfer it to a 250-ml conical flask that has been swept free of carbon dioxide. Add 50 ml of water (25 to 28°) that is free from carbon dioxide, stopper the flask, and shake gently until the sample is dissolved. Titrate to a *p*H of 8.6 with an approximately 0.1 *N* standard solution of sodium hydroxide free from carbonate, taking precautions to exclude carbon dioxide and using as an indicator either a *p*H meter of the glass-electrode type or two drops of a 0.5 per cent phenolphthalein solution. In the latter case, the end point can be determined by comparison with the color of a buffer solution (8.6) prepared as follows: mix 25 ml of 0.2 *M* H_3BO_3-KCl solution with 6 ml of 0.2 *M* NaOH; add two drops of 0.1 per cent phenolphthalein solution, and dilute to 100 ml with water free of carbon dioxide.

Determine the quantity of sodium hydroxide required to produce the end point by matching the color in another flask containing the indicator and the same volume of solution free of carbon dioxide. Subtract the amount required from that used in the first titration and calculate the

value of the alkali solution on the basis of the equation

$$KHC_8H_4O_4 + NaOH \rightarrow KNaC_8H_4O_4 + H_2O$$

Exercise 25.7. Determination of the Concentration of Sulfuric Acid

Solutions of any of the common, highly ionized acids can be titrated by means of sodium hydroxide, with any one of a number of indicators. The less highly ionized acids, such as those having ionization constants of the order of 10^{-5}, can be titrated similarly, but an indicator must be selected the *p*H range of which is in the general region of 6 to 10. In the case of orthophosphoric acid, methyl orange serves for titrating the first hydrogen, and phenolphthalein for the first two; the third hydrogen is not directly titratable, as mentioned in Chapter 13.

The Sample

Selection. To sample liquids of relatively small volumes it is usually necessary only to shake or stir them in order to secure thorough mixing so that a representative sample may be obtained. Take whatever precautions are necessary to achieve this objective.

Measurement. (a) If the results are to be reported in percentage by weight, weigh 5 to 10 g of acid in a weighing bottle (*1*). (b) If the results are to be reported in grams per unit volume, use a pipet to measure a suitable amount.

Treatment. Transfer the measured sample to a volumetric flask of such size that the titration of the selected aliquot, such as 25 ml, will require a reasonable volume of standard hydroxide (*2*). Dilute to the graduation mark and mix.

The Desired Constituent

Measurement. Titrate 25-ml portions of the diluted acid, using methyl orange, methyl red, or phenolphthalein as the indicator. Calculate the results as directed, using the standardization value for the hydroxide corresponding to the indicator selected (*3*).

NOTES: (1) Do not weigh beyond the third decimal place. Why?

(2) Whenever possible, the errors in reading the buret should be kept negligible by using a large enough volume of titrant.

(3) If desired, the acid may be put in the buret and used to titrate measured portions of the hydroxide solution. Using a buret for each solution enables one to titrate back and forth readily if the end point is accidentally passed.

Exercise 25.8. Determination of the Acidity of Vinegar

The reaction of hydroxide with vinegar may be taken as an example of the titration of a relatively weak acid. Most of the acidity of vinegars is due to acetic acid. The Federal standard requires not less than 4 g of this acid per 100 ml of vinegar. Malic acid makes up a small percentage of cider vinegar. Titration with a standard alkaline solution serves to determine the total acidity.

A complete chemical examination of vinegar entails the determination of various other constituents.[12]

The Sample

Selection. Observe the usual precautions for sampling a liquid.

Measurement. (a) If the results are to be reported in percentage by weight, weigh about 5 g in a stoppered weighing bottle (*1*). (b) If they are to be on the basis of grams of acetic acid/100 ml, secure 10.00 ml with a pipet.

Treatment. Transfer the sample to a 100-ml volumetric flask, dilute to the mark with boiled and cooled water (*2*), and mix.

The Desired Constituent

Measurement. Transfer a 25-ml portion to a conical flask, dilute with an equal volume of boiled water (*3*), add a drop of phenolphthalein indicator solution, and titrate with the standard hydroxide. Calculate the results as directed. Use the standardization value obtained on titrating acid with hydroxide, using phenolphthalein as the indicator.

NOTES: (1) If the vinegar is dispensed in a sealed ampoule or drawn-out test tube, break the tip of the container, empty the sample into a weighing bottle, and insert the glass stopper immediately. Avoid adding pieces of broken glass.

(2) Before the final dilution, the flask and solution should be at room temperature.

(3) This dilution, with that accomplished on preparing the solution, reduces the natural color to a point where (ordinarily) it will not interfere with observation of the indicator color change.

Exercise 25.9. Determination of Boric Acid

In a previous section it was stated that acids having low ionization constants cannot be titrated with satisfactory accuracy. Boric acid is such a compound. However, the addition of certain polyhydroxy organic compounds to a solution of boric acid causes it to function like an acid having a considerably higher ionization constant (*1*). Potentiometric titration

[12] Assoc. Offic. Agr. Chemists, *Methods of Analysis*, p. 487 (1950).

curves determined in the presence of a number of these compounds showed [13] the extent to which steep portions were produced in the curves. Of the substances tried, glycerol, mannitol, and invert sugar are recommended. Figure 13.2 (page 205) shows the effect of mannitol.

The determination of boron in commercial borax serves to illustrate this application. Borax reacts with hydrochloric acid according to the equation

$$2\ HCl + Na_2B_4O_7 \rightarrow H_2B_4O_7 + 2\ NaCl$$

The pyroboric acid reacts with water to form the ortho acid

$$H_2B_4O_7 + 5\ H_2O \rightarrow 4\ H_3BO_3$$

To the orthoboric acid thus formed in the solution is added the polyhydroxy compound. In the case of glycerol it has been suggested that a compound is formed having some such formula as $C_3H_5OH \cdot BO_3H$. On titration with a hydroxide this complex may be assumed to react according to the equation

$$C_3H_5OH \cdot BO_3H + NaOH \rightarrow C_3H_5OH \cdot BO_3Na + H_2O$$

The Sample

Selection and preparation. Procure a representative sample of commercial material, taking precautions necessary for such substances (*2*).

Measurement. Weigh by difference about 2.5 g of the material as received (*2*).

Treatment. Dissolve the sample in a 250-ml volumetric flask, dilute to the mark, and mix.

The Desired Constituent

Measurement. Transfer a 25-ml portion to a conical flask, and add a drop of methyl orange indicator solution. Titrate with a standard acid just to the end point (*3*).

To each of several other 25-ml portions of the sample solution add exactly the amount of standard acid determined in the above titration, but without any indicator. Boil the solution gently (*4*) and then cool it (*5*). Add 50 ml of a 1:1 mixture of glycerol (*6*) and water that has been neutralized with sodium hydroxide (*7*). After adding a drop of phenolphthalein solution, titrate with standard hydroxide. Calculate the results in terms of percentage of boric anhydride B_2O_3.

NOTES: (1) The formation of this type of complex frequently gives rise to an increased degree of ionization.

[13] Mellon and Morris, *Ind. Eng. Chem.* **16**, 123 (1924).

(2) Borax, $Na_2B_4O_7 \cdot 10\ H_2O$, may lose some water of crystallization if the conditions are unfavorable. The sample should not be dried.

(3) This gives the amount of standard acid required to liberate the boric acid.

(4) Boiling removes the carbon dioxide that would affect the phenolphthalein end point.

(5) The flask may be cooled in running water.

(6) If it is more convenient, 1 g of mannitol instead of the glycerol may be added to the solution before titration.

(7) Commercial glycerol must be tested for neutrality. It is usually acidic. The amount needed should be neutralized with sodium hydroxide by adding an equal volume of water and two drops of phenolphthalein solution and then titrating with dilute sodium hydroxide solution until the solution turns a faint pink. Avoid stirring in much air as the appearance of the pink hue becomes difficult to detect in the viscous mixture.

Exercise 25.10. Determination of the Alkalinity of Limestone

The determination of the alkalinity of limestone may be taken as an example of a case in which it is desirable to add an excess of one standard solution and titrate back with another solution.

If hydrochloric acid and sodium hydroxide are used as titrants, the equations involved are

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$
$$HCl + NaOH \rightarrow NaCl + H_2O$$

The Sample

Selection and preparation. Select a representative sample and grind it to a suitable degree of subdivision, such as 100-mesh.

Measurement. Weigh accurately samples of about 0.5 g and transfer them to 250-ml conical flasks.

Treatment. To each flask add 75 ml (*1*) of standard acid which is approximately 0.5 *N* (*2*). Attach the flask to a reflux condenser with a rubber stopper and boil gently for 30 minutes to dissolve the sample and expel carbon dioxide. Then wash down the condensed acid in the condenser, on the stopper, and on the walls of the flask.

The Desired Constituent

Measurement. Titrate the excess acid with a standard hydroxide solution using methyl orange as the indicator (*3*). Calculate the percentage of calcium carbonate in the sample (*4*).

NOTES: (1) If the sample were 0.5 g of pure calcium carbonate, how many ml of 0.5 *N* acid would just react with it?

(2) Half-normal acid makes the process of dissolution more rapid. Why?

(3) Other indicators may be used if the corresponding normality of the hydroxide is taken into account.

(4) How will the percentage be affected if part of the sample is magnesium carbonate?

Exercise 25.11. Determination of Nitrogen (Kjeldahl Method)

Nitrogen is one of the elements determined thousands of times a day in industrial and research laboratories. To determine the element as it occurs in mixtures containing ammonium salts, nitrates, or organic nitrogen compounds the method of Kjeldahl [14] is very generally used. The process consists essentially in decomposing the sample by boiling with concentrated sulfuric acid. Ultimately, organic material is destroyed and the nitrogen is fixed as ammonium sulfate in the excess acid. When the latter is neutralized with sodium hydroxide and an excess is added to metathesize ammonium sulfate to ammonium hydroxide, the ammonia may be distilled into a measured excess of standard acid. The excess acid is then titrated.

Some analysts[15] recommend distilling the ammonia into excess orthoboric acid. Because of the acid's small ionization constant, the ammonium salt formed may be titrated directly with strong acid. Accordingly, the boric acid solution need not be standardized.

In the application of this method various modifications are necessary or desirable for certain kinds of samples. Thus, the addition of certain catalytic agents decreases the time required for decomposition with acid. Gunning improved the process by adding potassium sulfate to raise the boiling point of the digestion mixture. For details regarding these modifications, see the references cited.[16]

Samples containing nitrates cannot be digested by the original method because of possible volatilization of some nitric acid. Salicylic acid may be added to prevent such loss. According to some writers, the nitric acid is fixed by a reaction represented by the equation

$$C_6H_4 \cdot OH \cdot COOH + HNO_3 \rightarrow C_6H_3 \cdot OH \cdot NO_2 \cdot COOH + H_2O$$

Addition of zinc then causes reduction to the corresponding amine, which may be handled in the usual way.

Apparatus

Obtain from the stock room the equipment necessary for a distillation assembly similar to that illustrated in Figure 25.2. The following main

[14] Kjeldahl, *Z. anal. Chem.* **22**, 366 (1883).

[15] See Ma and Zuazaga, *Ind. Eng. Chem., Anal. Ed.* **14**, 280 (1942).

[16] Stubblefield and De Turk, *Ind. Eng. Chem., Anal. Ed.*, **12**, 396 (1940); Assoc. Offic. Agr. Chemists, *Methods of Analysis*, p. 11 (1950).

parts are shown: tripod and wire screen; distillation flask, preferably the Kjeldahl pear-shape design; trap between distillation flask and condenser; water-cooled condenser; adaptor tube; and 500-ml conical receiving flask. A suitable support, with clamp, is needed to hold the condenser.

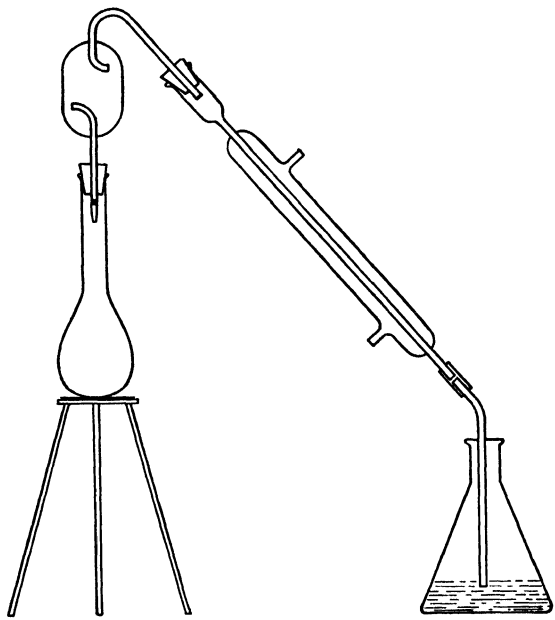


Figure 25.2

Arrangement of distillation apparatus.

The Sample

Selection and preparation. Select a representative sample and reduce it to a suitable state of subdivision. Most inorganic materials can be ground. Various fibrous organic substances may be subdivided in a Wiley mill. In either case the material must be reasonably dry for milling.

Measurement. Weigh about 1 g for materials relatively low in nitrogen. Smaller amounts suffice when the percentages are high (*1*).

Blank experiment. Unless it is known that the reagents are free of nitrogen, a blank determination should be made on a 1-g sample of sucrose by the regular procedure.

Treatment. Transfer the samples to dry 500-ml Kjeldahl digestion

flasks (*2*). Add 30 ml of concentrated sulfuric acid (*3*); in the operation, wash down any particles of sample adhering to the neck of the flask. Add about 0.3 g of cupric sulfate or selenium as a catalyst (*4*). Unless salicylic acid has been added to provide for nitrate nitrogen (*5*), incline the flask at an angle of 30 to 45° in a hood or place it on a Kjeldahl digestion rack (*6*). Heat gently at first and then gradually bring the temperature to boiling. Keep the acid boiling gently until coloration from organic matter disappears (*7*). Turn the flask occasionally to aid in bringing the acid into contact with undigested material (*8*). After the solution loses its amber or yellowish color, digest for 20 min. more. If the total volume drops below 15 ml, add 10 ml more of sulfuric acid. In no case should the volume exceed 25 ml when it is through digesting.

When the flask has stood long enough to cool (*9*), incline it at about a 45° angle and pour *carefully* 200 ml of water down the neck. Mix and cool again.

The Desired Constituent

Separation. Connect the Kjeldahl flask, as shown in Figure 25.2, to a condenser (*10*) that has been steamed out (*11*). Secure the flask in a vertical position with a trap between it (*12*) and the condenser to prevent spray being carried over. Pipet 50 ml of standard acid (*13*) into a 500-ml conical flask and place it so that the tip of the glass delivery tube of the condenser dips just below the surface of the solution. Add two drops of methyl red indicator to the acid, and have the laboratory assistant check the apparatus.

Add 100 ml of a 10 *N* solution of sodium hydroxide (*14*) to the distillation flask (*15*), preventing mixing as far as possible. Add at once about 1 to 2 g of mossy zinc (*16*) and connect the flask immediately with the condenser. Swirl the contents of the flask carefully (*17*) until the solutions are thoroughly mixed. Maintain a steady heating to prevent sucking the receiving acid back into the evolution flask. Start to heat *immediately*. Distill over about 150 ml of solution. Lower the receiving flask to bring the end of the delivery tube above the surface of the solution, remove the flame, and wash out the condenser and the delivery tube into the flask.

Measurement. Titrate with standard sodium hydroxide (*18*). Calculate the percentage of nitrogen in the sample, taking into account any correction obtained in the blank determination.

NOTES: (1) Too much sample may yield more ammonia than the standard acid will neutralize.

(2) If the flasks are supported vertically, little of the sample will stick in the neck.

Some analysts prefer to wrap the sample in a small filter paper and then put both into the flask.

(3) If the sample contains nitrate, nitrite, or nitro compounds, 2 g of salicylic acid should be included with the sulfuric acid.

(4) If metallic selenium is used as the catalyst, 0.2 g is sufficient. For the use of mercuric oxide in this capacity see the references.

(5) If salicylic acid has been added, let the mixture stand 30 min. and then add 2 g of zinc dust to reduce the nitro compounds formed. After heating slowly until frothing ceases, boil until white fumes are no longer evolved and then continue as in the regular procedure.

(6) Fumes from this mixture, along with water vapor, are very corrosive for ducts made of sheet iron. A Duriron installation is very satisfactory.

(7) The solution will be somewhat blue from cupric sulfate, if that catalyst is used.

(8) Samples vary greatly in the length of time required for digestion.

(9) If the system solidifies on cooling, the soluble material will dissolve when water is added.

(10) In routine laboratories special apparatus consisting of banks of digesters and stills is used. For individual work, the condenser recommended is convenient.

(11) Generate steam by boiling water and pass it through the condenser tube without the condensing water being turned on.

(12) Kjeldahl cylindrical traps are suitable.

(13) Preferably, it should be 0.2 *N*.

(14) To prepare the solution, saturate water with sodium hydroxide, stir well, allow to settle 6 hrs., siphon off the clear solution, and dilute (3:2) with water.

(15) Sodium hydroxide must be present in excess. When the solutions are mixed, this point will be indicated by the formation of a blue color with the cupric sulfate used as a catalyst. Phenolphthalein cannot be used, as strong alkali decolorizes it.

Alkali hydroxides precipitate cupric hydroxide, soluble in excess to give the deep blue ion, $Cu(OH)_4^{-2}$. This complex decomposes on boiling of the solution, with precipitation of black cupric oxide.

(16) Interaction of zinc and excess sodium hydroxide evolves hydrogen, which helps to prevent excessive bumping during distillation. Crushed porcelain may be used, and steam distillation is better yet.

(17) A student who is careless at this point may see his solution bound rapidly ceilingward.

(18) If the end point is overrun, add 5.00 ml more of standard acid.

CHAPTER 26

OXIDATION-REDUCTION METHODS[1]

Oxidimetry

Oxidimetry includes the methods in which standard oxidants are used to measure reducing substances. The latter may be the desired constituents themselves, or they may represent an excess of standard reductant. When constituents cannot be titrated directly, a back titration may be feasible, just as in neutralimetry. Several of the more commonly used procedures are given below as examples of the wide applicability of this type of titrimetric measurement.

PERMANGANIMETRY

In permanganimetry the permanganate ion is the essential oxidant. Since the oxidation potential of permanganate is relatively high, this oxidant can be used to oxidize quantitatively a large variety of substances that have sufficiently lower oxidation-reduction potentials. Such substances must exist in, or be convertible to, a known lower state of oxidation prior to titration with the permanganate.

Solutions and Standards

For all direct titrations, a standard solution of potassium permanganate is used. Reference to Table 14.1 (page 223) shows that, depending on the reaction involved, the equivalent weight may be one-third, one-fourth, or one-fifth of the molecular weight, or even the latter itself. The particular oxidation change undergone by the manganese of oxidation number 7 will be determined by the experimental conditions, e.g., the acidity or alkalinity of the solution. Permanganate is most commonly used in acidic solution under conditions where the oxidation number of the manganese changes from 7 to 2. Since this compound is not a primary stand-

[1] See Chapters 12 and 14 for a general discussion of this subject.

ard, the solution must be standardized, preferably by checking against N.B.S. sodium oxalate. The reaction proceeds according to the equation[2]

$$2\ MnO_4^- + 5\ C_2O_4^{-2} + 16\ H^+ \rightarrow 2\ Mn^{+2} + 10\ CO_2\uparrow + 8\ H_2O$$

from which it is evident that one-half the molecular weight of sodium oxalate is the equivalent weight. (Divide the equation by 10 to obtain the equivalent weight.)

In order to compensate errors it is best, in some cases, to standardize a solution against the substance to be determined and under the same conditions. This practice is recommended when permanganate is used for determining calcium, via precipitation as the oxalate and titration of the oxalate ion.

When standard ions of reducing substances are used for back titrations with potassium permanganate, a solution of ferrous ammonium sulfate containing sulfuric acid, or of arsenious oxide containing sodium hydrogen carbonate, is generally employed. Preferably the ferrous solution should be checked against the standard permanganate, the ionic reaction being

$$MnO_4^- + 5\ Fe^{+2} + 8\ H^+ \rightarrow Mn^{+2} + 5\ Fe^{+3} + 4\ H_2O$$

The best grade of ferrous ammonium sulfate is often surprisingly close to 100 per cent purity, but it is not recommended as a primary standard. In any case, ferrous solutions are not stable. Arsenious oxide may be secured from the National Bureau of Standards for the arsenite solution. Its reaction with permanganate in acidic solution is

$$5\ AsO_3^{-3} + 2\ MnO_4^- + 6\ H^+ \rightarrow 5\ AsO_4^{-3} + 2\ Mn^{+2} + 3\ H_2O$$

Applications

Of the numerous constituents that may be determined by means of permanganate[3] only three are considered here. Other selections serve as well.

For certain determinations this oxidant is not as popular as formerly. However, the solution has a high oxidation potential and its self-indicating properties are exceptional. The solution is not easily prepared or preserved. Troublesome side reactions may produce fading end points, as in the determination of iron in ores dissolved in hydrochloric acid. After oxidation of the iron (II), excess permanganate reacts slowly with the chloride ions. The discovery of satisfactory internal indicators for use with dichromate and cerate makes these oxidants preferable in some respects to permanganate.

[2] For a discussion of the complicated nature of this reaction, see Malcolm and Noyes, *J. Am. Chem. Soc.*, *74*, 2769 (1952).

[3] See Treadwell-Hall, *Analytical Chemistry*, Vol. II, pp. 534-575, Wiley, 1942.

Exercise 26.1. Preparation of Standard Solution of Potassium Permanganate

On the basis of the equation for the half-cell electrode reaction in acidic solution

$$Mn^{+2} + 4\ H_2O \rightleftarrows MnO_4^- + 8\ H^+ + 5\ e$$

calculate the amount (*1*) of potassium permanganate required for 1 liter of 0.1 *N* solution (*2*). Weigh approximately the amount calculated, transfer to a 1-liter, glass-stoppered bottle, nearly fill it with water, and shake to aid dissolution (*3*).

Allow the solution to stand, for reaction with any oxidizable material that may be present (*4*). At room temperature this action may require a week, whereas at 70° a few hours will suffice (*5*). Some analysts recommend boiling for 10 to 15 min. In order to remove the precipitate of manganese dioxide that appears, arrange a suction filtering device according to the instructor's advice, using either a funnel with a sintered glass bottom or a perforated porcelain crucible containing a mat of asbestos on the bottom (*6*). Pour the solution through the filter (*7*), receiving it preferably in the container in which it is to be stored (*8*). If the solution is being taken out of a volumetric flask, the vessel may be secured in a vertical position with the neck touching the surface of the solution in the filter in such a way that the solution runs out at the same rate as it goes through the filter.

To standardize the solution, calculate the amount of sodium oxalate that will require 35 to 40 ml of the permanganate solution. Dry the oxalate at 105°, weigh out separate portions (*9*), and transfer to 600-ml beakers. Dissolve and titrate one-at-a-time as follows:

Add 250 ml of dilute sulfuric acid (12.5 ml concentrated acid diluted to 250 ml) which has been recently boiled for 10 to 15 min. and then cooled to 27 ± 3°. Stir until the oxalate has dissolved. Add about 30 to 35 ml of the permanganate solution in a steady stream over a period of about 75 seconds while stirring slowly. After the pink color disappears (about 45 sec.) (*10, 11*), heat the solution to 55 to 60° (*12*). Complete the titration by slowly adding permanganate solution until a faint pink color persists for about 30 sec. Add the last 0.5 to 1 ml dropwise, with particular care to allow the solution to become decolorized before the next drop is added.

Determine the excess of permanganate solution required to impart the permanent pink color to the solution by adding permanganate to the same volume of the specially treated dilute sulfuric acid heated to 55 to 60°. This correction usually amounts to 0.03 to 0.05 ml.

Calculate the normality of this solution and its titers in terms of the constituents for which it is to be used (*13*).

NOTES: (1) If the solution is to be diluted to a definite concentration, sufficient excess should be taken to allow for impurities and for making enough solution with which to perform preliminary titrations.

(2) The meniscus on 0.1 *N* solutions is difficult to read in 50-ml burets. A small light held behind the buret is helpful. Some analysts prefer to read the top of the meniscus.

(3) Should the solution be standardized at once, care must be taken to have all the permanganate dissolved.

(4) This procedure should be followed if the solution is to be preserved any length of time. If it is to be used immediately and but once after standardization, the standing and removal of manganese dioxide may be omitted.

(5) The reaction in neutral solution with reducing matter produces manganese dioxide as a precipitate. Since the latter compound seems to function catalytically to accelerate further decomposition of the permanganate ($4\ KMnO_4 + 2\ H_2O \rightarrow 4\ MnO_2\downarrow + 4\ KOH + 3\ O_2\uparrow$), the precipitate must be removed if the solution is to be kept any length of time without frequent restandardization.

(6) See page 471 for instructions for preparing Gooch crucibles.

(7) The apparatus should be such that the solution does not come in contact with organic matter.

(8) The permanganate container should be rinsed out with a little of the filtered solution.

(9) The laboratory stock may be checked against the N.B.S. material and a purity factor applied if necessary.

(10) The reaction gets under way slowly and seems to be catalyzed by the reduction products formed.

(11) If the pink color should persist because the equivalence point has been passed owing to the permanganate's being too strong, discard this titration; start again, but use less of the permanganate solution in the initial portion

(12) Earlier heating to this temperature decomposes some oxalate.

(13) Checking determinations should come close to 1 part in 1000.

Exercise 26.2. Determination of Oxalic Acid

Oxalic acid is interesting titrimetrically in that it is sufficiently ionized as an acid in solution to make a titration possible with a strong base, with phenolphthalein as the indicator; or the oxalate ion may be titrated with a suitable oxidant, such as potassium permanganate.

The Sample

Selection and preparation. Select what seems to be a representative sample of the commercial material at hand. If any grinding or drying is necessary for preparing it, care must be exercised not to lose any of the water of crystallization.

Measurement. Weigh out separate portions (*1*), or a single portion large enough to provide suitable aliquots when dissolved.

Treatment. Transfer the material to 500-ml conical flasks and dissolve the separate portions in about 50 ml of water. If one large portion is used, dissolve and dilute to 250 ml.

The Desired Constituent

Measurement. To the solution of the separate portion, or to an aliquot of 25 ml, add 10 ml of a mixture of 140 ml of water and 10 ml of concentrated sulfuric acid. Heat the solution to $27 \pm 3°$ and titrate in the same manner as in the standardization of the permanganate against sodium oxalate. Calculate the percentage of oxalic acid dihydrate.

NOTE: (1) Assuming pure acid, $H_2C_2O_4 \cdot 2\,H_2O$, what weight of sample would require 35 ml of 0.1 *N* permanganate solution?

Exercise 26.3. Determination of Hydrogen Peroxide

Hydrogen peroxide may react either as an oxidizing or reducing agent. When functioning in the former capacity, the half-cell reaction is

$$2\,H_2O \rightleftarrows H_2O_2 + 2\,H^+ + 2\,e$$

In the oxidation of iodide the reaction proceeds according to the equation

$$2\,I^- + H_2O_2 + 2\,H^+ \rightarrow I_2 + 2\,H_2O$$

As a reducing agent the half-cell reaction is

$$H_2O_2 \rightleftarrows O_2\uparrow + 2\,H^+ + 2\,e$$

With permanganate, the reaction is

$$2\,MnO_4^- + 5\,H_2O_2 + 6\,H^+ \rightarrow 2\,Mn^{+2} + 5\,O_2\uparrow + 8\,H_2O$$

The Sample

Selection. Shake a bottle of commercial material to insure uniformity of the solution.

Measurement. Pipet 25 ml of commercial solution into a 250-ml volumetric flask (*1*). Dilute the solution to the graduation mark with water and mix the contents of the flask.

The Desired Constituent

Measurement. Transfer 25 ml of the prepared solution to a conical flask, dilute to about 100 ml with water, add 10 ml of 9 *M* sulfuric acid,

and titrate with the permanganate solution to the first permanent pink coloration (*2*).

Calculate the amount of hydrogen peroxide as directed, and report the percentage either by weight or by volume (*3*).

NOTES: (1) The common commercial solution is supposed to be 3 per cent hydrogen peroxide.

(2) If the first drop of permanganate causes a permanent pink coloration, not enough acid is present or the peroxide has decomposed

(3) If the percentage is reported by volume, it indicates the number of milliliters of oxygen that can be obtained from 100 ml of the original solution, the decomposition taking place according to the equation

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2\uparrow$$

The calculation may be made for 0° and 760 mm. "Ten-volume" hydrogen peroxide will evolve ten times its own volume of oxygen.

Exercise 26.4. Determination of Calcium

In the oxidimetric determination of calcium, the element is separated by precipitation as the oxalate, filtered, washed to remove excess oxalate ion, and dissolved in sulfuric acid. The resulting oxalate ion is then titrated with permanganate which reacts according to the equation on page 422.

In addition to giving experience in using a precipitation-titrimetric procedure, the method illustrates the practice of standardizing the titrant under the conditions of use. In this case a sample of calcium carbonate of known purity is carried through the same procedure as the unknown sample.

The Sample

Selection and preparation. Secure and prepare in the usual manner a sample of the material to be analyzed. It is assumed that no constituents will be present that would interfere with the separation of the calcium by precipitation.

Measurement. Weigh on watch glasses two or three samples each of the unknown and of the standard calcium carbonate, taking about 0.2 g in each case. Transfer to marked 400-ml beakers.

Treatment. Add about 75 ml of water, cover with a watch glass, and add 10 ml of 10 per cent hydrochloric acid. When the sample dissolves, boil the solution 1 to 2 min. to expel carbon dioxide (*1*). Rinse down the inside of the beaker and the cover glass, and dilute to about 200 ml.

The Desired Constituent

Separation. Add two drops of methyl red indicator and then 20 ml of a freshly prepared (*2*) saturated solution of ammonium oxalate (*3*). Next, add 10 g of urea and heat the solution to boiling. Maintain this temperature in order to hydrolyze the urea to ammonia and carbon dioxide, and thus to neutralize the free acid (see Exercise 28.5). When the indicator hue changes to yellow, remove the beaker from the hot plate.

When the supernatant liquid is clear, test for completion of precipitation by adding a few drops of ammonium oxalate solution. Do not begin the next operation unless there is time to complete the determination (*4*).

Filter the solution through a No. 42 Whatman (or equivalent) paper, transferring as much as possible of the precipitate from the beaker to the paper. Rinse the beaker three times with 5-ml portions of a 0.1 per cent solution of ammonium oxalate (*5*) to complete transferring the precipitate. Wash the precipitate on the paper thoroughly with 5-ml portions of the washing solution, allowing the paper to drain between washings. Complete the washing with four 4-ml portions of cold water (*6*) and rinse the beaker. Reject the filtrate.

Under each funnel place the beaker from which the respective precipitate was transferred. Pierce the tip of the paper with a stirring rod that has its end drawn to a point, and wash the precipitate into the beaker with a stream of hot water. Dissolve any remaining precipitate by pouring over the paper three 5-ml portions of hot, 25 per cent (4.5 *M*) sulfuric acid. Complete the washing with hot water, but do not discard the filter paper. The volume of solution should be approximately 75 ml.

Measurement. Add a mixture of 125 ml of water and 7 ml of concentrated sulfuric acid. Heat to 30°. Run in about 30 ml of permanganate solution at a rate of about 20 to 25 ml per minute while stirring slowly. Let stand for about 45 sec. (the pink color may disappear). Heat to 55 to 60°. Place the paper used in the filtration in the solution and stir. When the pink color has been discharged, complete the titration. Disregard a slow fading of the pink color (*7*).

Calculate the normality and calcium titer of the potassium permanganate solution, making correction for the purity of the calcium carbonate used as a standard. Using the average value so obtained, calculate the percentage of calcium in the unknown (*8*).

NOTES: (1) If carbon dioxide is not expelled, what may happen at this point? In such a case, acidify the solution again, boil, and once more make it alkaline.

(2) On standing, a solution of ammonium oxalate decomposes somewhat with the formation of some carbonate. What would be the effect?

(3) Dissolve about 4 g of ammonium oxalate in 100 ml of water.

(4) The precipitates may be allowed to stand at this point in the locker until the next laboratory period, provided there is no magnesium to co-precipitate.

(5) What advantage has this solution as a washing medium?

(6) Why change the washing medium? What advantage has cold water?

(7) Potassium permanganate is reduced by fine shreds of paper.

(8) It is evident that one titrates the oxalate ion and then assumes that each oxalate ion was associated with one atom of calcium.

DICHROMATIMETRY

The procedures grouped together in dichromatimetric methods are based upon reactions in which the dichromate ion is the oxidant. Potassium dichromate is used to prepare the standard solution. It is employed for oxidations in acidic solution.

Although potassium dichromate is limited by having an oxidation potential 0.2 volts lower than that of potassium permanganate, it has a distinct advantage in being a primary standard and in giving aqueous solutions which are stable indefinitely. The color of the tervalent chromium formed may complicate the visual detection of certain end points.

Solutions and Standards

As stated, potassium dichromate is a primary standard and can be weighed directly. A number of investigations have shown that the usually obtainable material cannot safely be assumed to have the composition represented by the formula, $K_2Cr_2O_7$. Careful checking of finely ground commercial salt against an N.B.S. iron ore will give a purity factor that can be used. For a number of batches the author has obtained a value in the neighborhood of 1.005. This shows a small excess oxidizing capacity, in terms of the formula.

The salt may be recrystallized readily from water. A product obtained from three recrystallizations and well dried may be used directly for most good analytical work.

In case it is desired to standardize the solution, several methods are available.[4]

Applications

In comparison with the number and variety of procedures given for potassium permanganate in reference works, usually only a few are suggested for potassium dichromate. The methods for iron, chromium, and uranium are given here.

[4] Treadwell-Hall, *op. cit.*, pp. 575-583.

Exercise 26.5. Preparation of a Standard Solution of Potassium Dichromate[5]

Calculate the amount of potassium dichromate required (*1*) for 500 ml of a solution, each milliliter of which will be equivalent of 0.005000 g of iron (*2*). Weigh on a watch glass material dried at 105°, transfer to a 500-ml flask, dissolve in water, and dilute to the mark.

NOTES: (1) Take into account the determined or assumed purity of the salt.
(2) The half-cell reactions involved in determining iron with dichromate are

$$2\ Cr^{+3} + 7\ H_2O \rightleftarrows Cr_2O_7^{-2} + 14\ H^+ + 6\ e$$
$$Fe^{+2} \rightarrow Fe^{+3} + 1\ e$$

Exercise 26.6. Determination of Iron in an Iron Ore

In addition to being stable and functioning as a primary standard, potassium dichromate has a specific advantage over permanganate for determining iron in that it is not appreciably reduced by hydrochloric acid, generally the preferable solvent for iron ores.

On dissolution in hydrochloric acid most of the iron is in the ferric state. It must be reduced to the ferrous state and any excess reducing agent either eliminated or separated. Titration is then made with the dichromate, the method given here being for the internal indicator sodium diphenylaminesulfonate $C_6H_5 \cdot NH \cdot C_6H_4 \cdot SO_3Na$. At a potential near 0.85 volts it is transformed from a colorless diphenylamine derivative to a derivative of diphenylbenzidine violet.

The Sample

Selection and preparation. Select a portion of ore representative of the carload, lot, or mine to be sampled, and grind it to 100-mesh size. Dry at 105° the part to be weighed.

Measurement. Weigh on a tared watch glass a sample of exactly 0.5000 g (*1*), and transfer to a porcelain crucible by means of a pencil brush. If desired, weigh directly in the crucible.

Treatment. Heat the uncovered crucible for 5 min. over a Bunsen burner to oxidize organic matter and then place it in a casserole to cool. Add 25 ml of concentrated hydrochloric acid, cover with a watch glass, and heat (hood) just to boiling until dissolution is complete, or no further action ensues (*2*). If the residue (*3*) contains no colored particles, transfer the solution to a 500-ml conical flask, and proceed according to the directions in the third paragraph below.

[5] N.B.S. standard sample No. 136 is available.

If an appreciable amount of colored material remains undissolved, it may contain iron. Filter the solution on paper into a 500-ml conical flask. Wash the paper with hot water until it is *free* of yellow ferric iron. Cover the flask with a watch glass and set aside.

Burn the paper in a porcelain crucible (*4*) by heating slowly until all black carbonaceous material disappears. Add about 5 g of potassium pyrosulfate to the residue in the crucible and heat carefully to fuse the mass (*5*). Maintain at a temperature just sufficient to keep the system liquefied until no further action takes place (*6*). Allow the fused mass to cool, and add a few milliliters of water containing a little hydrochloric acid. When the fused mass is loose in the crucible, transfer all the contents to the 500-ml conical flask previously set aside.

Add a few glass beads to the flask, boil to dissolve the cake, and evaporate to about 50 ml (*7*). *From this point on, complete each determination before beginning the next one* (*8*). Do not start this step unless there is sufficient time to complete the determination. While swirling the flask containing the hot solution, add dropwise from a pipet a solution of chlorostannous acid (*9*) until the ferric ion is just reduced (*10*), as shown by the disappearance of the yellow hue. Add two drops excess of reducant, and rotate the flask in running tap water to cool the solution quickly (*8*). When the solution is cool, add to it all at once (*11*) 25 ml of a 5 per cent solution of mercuric chloride and mix quickly. The precipitate of mercurous chloride should be white; it often has a beautiful silken appearance (*12*). Proceed at once with the next section.

The Desired Constituent

Measurement. Dilute the reduced solution to about 200 ml and add 15 ml of a special solution containing sulfuric and phosphoric acids (*13*). Add eight to ten drops of sodium diphenylaminesulfonate indicator (*14*) solution and titrate immediately with the dichromate solution. Reduction of the dichromate produces a green hue in the solution through the formation of tervalent chromium. The end point is marked by a rather quick change from a slate-blue to a violet hue. If the iron titer of the solution was 0.005000 and the sample was 0.5000 g, the milliliters of titrant equal the percentage of iron.

NOTES: (1) If the dichromate solution is made so that each milliliter is equivalent to 0.005000 g of iron, the use of 0.5000-g samples makes it read percentages directly.

(2) Some ores relatively insoluble in hydrochloric acid will dissolve on addition of enough chlorostannous acid to remove practically all the color of the ferric ion already dissolved. If an excess is added, this must be removed by adding carefully a *few* small crystals of potassium permanganate until a slightly yellow color appears.

(3) Most ores contain more or less insoluble siliceous material, which sometimes is slightly yellowish.

(4) Some ores do not give up their iron by the treatment recommended. In this case the paper should be burned in a platinum crucible. Then add to the residue in the crucible about 1 ml of hydrofluoric acid (*with care*) from the bottle, and heat gently (hood) to volatilize the excess. Then proceed with the fusion with pyrosulfate.

(5) The fusion causes a reaction represented by the equation

$$3\ K_2S_2O_7 + Fe_2O_3 \rightarrow 3\ K_2SO_4 + Fe_2(SO_4)_3$$

(6) Considerable time is required if much iron is present, as the process is slow. Release of iron is shown by an increasing depth of yellow color.

(7) The small volume is necessary to aid in detecting the completion of the subsequent reduction process.

(8) The reduced solution oxidizes rapidly.

(9) To prepare the solution of chlorostannous acid dissolve 110 g of c.p. "stannous chloride" in 170 ml of concentrated hydrochloric acid, add a few pieces of mossy tin, and dilute to 1 liter with water.

(10) The ionic equation for the reduction reaction is

$$2\ Fe^{+3} + SnCl_4^{-2} + 2\ Cl^- \rightarrow 2\ Fe^{+2} + SnCl_6^{-2}$$

The iron probably is present in a complex ion, such as $FeCl_4^-$.

(11) The desired reaction is expressed by the equation,

$$SnCl_4^{-2} + 2\ Hg^{+2} + 4\ Cl^- \rightarrow SnCl_6^{-2} + Hg_2Cl_2\downarrow$$

Insofar as possible, local excess of reductant should be prevented to avoid formation of metallic mercury, according to the equation

$$SnCl_4^{-2} + Hg^{+2} + 2\ Cl^- \rightarrow SnCl_6^{-2} + Hg\downarrow$$

This same undesirable reaction takes place if too much reducing agent is present when the mercuric chloride is added. Also, too much precipitated mercurous chloride interferes with the end point; or this compound itself may yield metallic mercury by reaction with excess chlorostannous ion, according to the equation

$$SnCl_4^{-2} + Hg_2Cl_2 \rightarrow SnCl_6^{-2} + 2\ Hg\downarrow$$

Whatever its source, metallic mercury functions as a reductant toward dichromate, whereas mercurous chloride does not.

(12) A gray precipitate indicates contamination with metallic mercury. Very much of it gives fading end points, and ruins the determination.

(13) The mixed acid contains 150 ml of concentrated sulfuric acid and 160 ml of 85 per cent phosphoric acid per liter. The use of the latter acid serves two purposes by forming a stable iron-phosphate complex species. First, the oxidation potential of the ferric-ferrous system is sufficiently lowered that the indicator (itself of relatively low oxidation potential) will be oxidized at the equivalence point and not before it. Secondly, the yellow color of ferric ion complex in hydrochloric acid solution is removed.

(14) The indicator solution is prepared by dissolving 0.30 g of sodium diphenylaminesulfonate in 100 ml of water.

Exercise 26.7 Determination of Chromium in Chromite

The determination of chromium in chromite, its most important ore, illustrates the use of a dichromate solution in a back titration. The chromite is first fused with sodium peroxide to oxidize the tervalent chromium to chromate:

$$2\ FeCr_2O_4 + 7\ Na_2O_2 \rightarrow 2\ NaFeO_2 + 4\ Na_2CrO_4 + 2\ Na_2O$$

On addition of water, and boiling, the excess peroxide is decomposed and the iron is precipitated:

$$NaFeO_2 + 2\ H_2O \rightarrow NaOH + Fe(OH)_3\downarrow$$

The addition of acid dissolves the precipitate and neutralizes the soluble base. Also dichromate is produced, according to the reaction

$$2\ CrO_4^{-2} + 2\ H^+ \rightarrow Cr_2O_7^{-2} + H_2O$$

The latter is then reduced with excess ferrous sulfate, according to the equation

$$Cr_2O_7^{-2} + 6\ Fe^{+2} + 12\ H^+ \rightarrow 6\ Fe^{+3} + 2\ Cr^{+3} + 6\ H_2O$$

and the excess is titrated back with a standard solution of dichromate.

The Sample

Selection and preparation. Reduce the selected sample of ore to a size to pass a 100-mesh screen.

Measurement. Weigh 0.25 g of the finely powdered ore and transfer to a 25-ml porcelain crucible (*1*).

Treatment. Mix the ore in the crucible with about 4 g of sodium peroxide (*2*) by means of the point of an iron nail. Spread over the top of the mixture about another gram of peroxide and leave the nail in the crucible. Place the crucible in a larger porcelain crucible and heat to the melting point of the flux by means of a low flame with the burner held in the hand. Maintain the fused mass in a liquid condition for at least 10 min. Stir it constantly with the nail held in crucible tongs. Allow the mixture to cool until a crust forms on the top, add another gram of peroxide, and fuse again for 5 min. Cool, place the inner crucible and the nail in a 400-ml beaker, cover with a glass and add carefully 75 ml of water. When the evolution of gas has ceased, rinse the nail and remove it. Boil 20 min. to decompose the excess peroxide, stirring to prevent bumping (*3*). Make the solution just acidic to litmus paper with 3 *M* sulfuric acid and then add 10 ml in excess. Boil for 10 min. to remove dissolved oxygen (*4*).

The Desired Constituent

Measurement. To the cold solution of approximately 200 ml add accurately weighed, pure ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$, in an amount such that there will be about 0.2 g more than enough to reduce the dichromate, on the assumption that the ore is pure chromite (*5*). Mix the solution well. Add 15 ml of the solution of mixed acids recommended in the previous determination (Note 13, Exercise 26.6) and 5 drops of the sodium diphenylaminesulfonate indicator solution. Back titrate the excess reductant with standard 0.1 *N* dichromate solution and calculate the percentage of chromium (*6, 7*).

NOTES: (1) A crucible of nickel or iron may be used, as porcelain crucibles are attacked somewhat in the fusion.

(2) Select only the yellow peroxide. Whitish material is sodium carbonate or hydroxide.

(3) The solution may be placed on the steam hot plate for 45 min. and stirred occasionally.

(4) The crucible may be removed but it will do no harm.

(5) The formula may be assumed to be $FeO \cdot Cr_2O_3$.

(6) A solution of ferrous ammonium sulfate may be used for the reduction. It should be standardized on the day it is used, by means of the same procedure used in the analysis.

(7) Calculate the number of milliliters of 0.1 *N* ferrous ammonium sulfate required just to reduce the chromium in a 0.4 g sample containing 25 per cent chromium.

Exercise 26.8. Determination of Uranium

Since the announcement of the atomic bomb, analytical interest in uranium has greatly increased. The following three methods have been much used to determine the element: *gravimetric,* by converting to the oxide, U_3O_8, and weighing as such; *colorimetric,* by converting to a yellow complex with hydrogen peroxide; and *titrimetric,* by oxidation from the quadrivalent to the sexivalent state.

The titrimetric method is included here as another example of the use of dichromate as an oxidant. The reaction is

$$3\ UO^{+2} + Cr_2O_7^{-2} + 8\ H^+ \rightarrow 3\ UO_2^{+2} + 2\ Cr^{+3} + 4\ H_2O$$

The sexivalent uranium obtained in the usual processes of dissolution of samples may be reduced to the quadrivalent state by different means. To illustrate the use of a metal as a reductant, amalgamated zinc is recommended here. Use is made of the Jones reductor. This reduction process yields a mixture of tervalent and quadrivalent uranium, but simple aeration gives a uniform quadrivalent product.

Since the oxidation reaction with dichromate is slow, use of a catalyst

is desirable to improve the end point. The ferric ion serves for this purpose, apparently through the rapid reaction

$$2\ Fe^{+3} + UO^{+2} + H_2O \rightarrow 2\ Fe^{+2} + UO_2^{+2} + 2\ H^+$$

The accompanying procedure[6] is somewhat involved in order to provide for possible interferences in ore and mineral analysis. Following decomposition with nitric and sulfuric acids, the sample is converted to sulfates by fuming. Heavy metals are separated with hydrogen sulfide; and iron, titanium, and others are separated by a chloroform extraction of the cupferrates. Following destruction of excess cupferron, the uranium is reduced, aerated, and titrated.

Apparatus

The apparatus usually used for a Jones reductor is illustrated in Figure 26.1. A suction flask should be used as a receiver for the reduced solution. The column of amalgamated zinc is about 2 cm in internal diameter and 30 cm long. A perforated porcelain plate, covered with glass wool, supports the zinc particles.

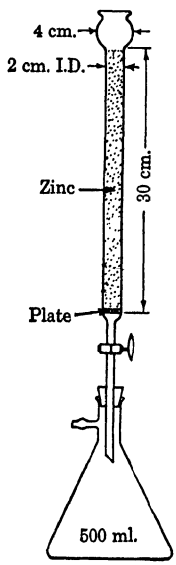


Figure 26.1
Zinc reductor.

To amalgamate the zinc (*1*), treat in a beaker 250 g of 20- to 30-mesh analytical grade metal with 250 ml of a solution containing 2 per cent mercuric nitrate and 1 per cent nitric acid. After stirring vigorously for 10 min., wash several times by decantation (*2*).

The reduction tube is first filled with water. Then the zinc is transferred to it until the column reaches the height shown in Figure 26.1. Use suction, if necessary, to pull the liquid through slowly, wash well with water, and finally leave the metal covered with water (*3*).

The Sample

Selection. Select a representative portion of the ore to be analyzed. It should be ground to pass a 100-mesh screen.

Measurement. Weigh a 2-g sample, transfer it to a 250-ml beaker, and moisten with water.

Treatment. Add 30 ml of nitric acid (1:1) and 12 ml of sulfuric acid (1:1). Cover with a watch glass and place on a hot plate at low heat

[6] Adapted, with permission, from the compilation, Rodden *et al., Analytical Chemistry of the Manhattan Project,* pp. 138-140, McGraw-Hill, 1950.

for 2 hrs. Tip the cover glass, continue heating for 1 hr., and then increase the heat until fumes of sulfur trioxide are evolved. Continue fuming 3 to 5 min., allow the mass to cool, and add 90 ml of water. Next, heat nearly to boiling to dissolve all soluble material.

The Desired Constituent

Separation of sulfides.[7] Transfer the solution to a 500-ml suction flask. Stopper the flask loosely and pass hydrogen sulfide under slight pressure in through the side arm for 30 min. Then close both neck and side arm and allow to stand overnight.

Filter the solution through a Whatman No. 40 paper into a 400-ml beaker, and wash the precipitate thoroughly with dilute sulfuric acid (1:19) that is saturated with hydrogen sulfide. Evaporate the filtrate to about 90 ml on a steam bath (*4*).

Separation of cupferrates. Add 10 ml of sulfuric acid (1:1) to the filtrate and heat the solution to boiling. Add dropwise a 2 per cent solution of potassium permanganate until the solution is permanently pink. Then cool the solution to below 5° in an ice bath.

Transfer the solution to a 300-ml separatory funnel, add 25 ml of a 6 per cent solution of cupferron, and shake the funnel for 1 min. Then add 25 ml of chloroform and shake the funnel for 1 min. (*5*). After the solutions separate, draw off the chloroform layer. Leave a little chloroform in the funnel to prevent loss of uranium with the aqueous layer.

Repeat this extraction until the chloroform layer is pale green (*6*) or colorless. Then add 5 ml of cupferron solution and shake the solution. If the precipitate is white and does not impart a brown color to the chloroform layer in the subsequent extraction, the separation is complete; otherwise, further extraction is necessary.

Separation of organic matter and nitrates (*7*). Transfer the aqueous layer from the separatory funnel to the original beaker, and wash the funnel twice with water. Add 15 ml of nitric acid and cover the beaker with a watch glass raised on glass hooks. Evaporate on a hot plate to heavy fumes of sulfur trioxide, and continue fuming for 3 to 5 min. Cool and wash down the cover glass and the beaker with at least 15 ml of water.

Add 1 ml of 60 per cent perchloric acid, cover, and again heat to fumes of sulfuric trioxide (*8*). Cool and wash down as before. Four such fumings are necessary to remove nitrates and organic material.

Following the final fuming, cool the solution, add 50 to 75 ml of water, and heat to dissolve the salts (*9*). Transfer the solution to a 200-ml

[7] See Rodden *et al., op. cit.,* pp. 14-44, for a summary of many methods of separation.

volumetric flask, add enough sulfuric acid to make the total sulfuric acid 5 per cent by volume after dilution, dilute to volume, and mix.

Measurement.[8] Transfer a suitable aliquot of the solution to a 250-ml beaker. Heat to boiling and oxidize by adding dropwise a 2 per cent solution of potassium permanganate until a permanent pink hue results (*10*). Cool the solution rapidly to room temperature by using an ice bath. Then pass the solution through a Jones reductor that has been previously washed with 5 per cent sulfuric acid, followed by water, at the rate of 30 to 40 ml per min. Wash the reductor with three 30-ml portions of sulfuric acid (1:19), followed by three 30-ml portions of water (*11*).

Transfer the reduced solution to a 600-ml beaker and aerate by passing a rapid stream of air through a glass tube into the solution for 5 to 10 min. (*12*). Remove the aeration tube and wash down the flask.

Add 20 ml of a freshly prepared 4 per cent solution of ferric chloride, stir, and add 15 ml of mixed sulfuric and phosphoric acids (*13*). Add eight drops of diphenylaminesulfonate indicator (*14*) and titrate immediately to a permanent purple hue with 0.5 *N* potassium dichromate solution.

Calculate the percentage of uranium in the sample (*15*).

NOTES: (1) Amalgamation of the zinc largely prevents the evolution of hydrogen.

(2) The particles should have a lustrous appearance.

(3) The zinc should be left covered with water to keep the column in the best working condition.

(4) If sulfides precipitate during evaporation, repeat the sulfide precipitation, washing, and evaporation.

(5) This is a good example of separation of interfering constituents by formation of compounds that are soluble in an immiscible liquid (chloroform, in this case).

(6) A greenish tint in the chloroform layer, even after complete extraction, comes from excess cupferron.

(7) Organic matter and nitrates must be eliminated before titration with dichromate.

(8) Consult the instructor regarding precautions necessary for such evaporations with perchloric acid.

(9) The solution should have 50 to 75 ml volume.

(10) One or two drops should suffice if all organic matter has been removed.

(11) A dark, olive-green hue characterizes tervalent uranium.

(12) Aeration brings over-reduced uranium back to the quadrivalent state, where the hue is clear emerald green.

(13) Add 150 ml of concentrated sulfuric acid to 350 ml of 85 per cent phosphoric acid.

[8] See Rodden *et al., op. cit.*, pp. 44-135, for a summary of the variety of methods available for measuring uranium.

(14) A 0.01 *M* solution of sodium diphenylaminesulfonate is used.

(15) Unless the dichromate is standardized in the same manner against a solution of known uranium content, a correction should be applied for dichromate consumed by reaction with the indicator.

IODIMETRY

Iodimetric methods are based upon the use of a standard solution of iodine as the oxidant. Although the E° value of iodine is only approximately −0.54 volts (much lower than that for permanganate, dichromate, or cerate solutions), it is sufficient for a number of important uses, such as the determination of sulfur and arsenic.

Iodine is not appreciably soluble in water alone; but in an aqueous solution of potassium iodide it dissolves readily, presumably with the formation of the triiodide ion I_3^-. In appearance the solution resembles iodine in ethanol. The triiodide ion results from the reversible reaction

$$I^- + I_2 \rightleftarrows I_3^-$$

Since reactions in which the I_3^- ion functions involve only two of the three iodine atoms in this ion, it may help to write the formula in the form $(I_2)I^-$. In reacting with a reductant, each of the two iodine atoms set apart in this formula takes on an electron, and hence serves as the oxidant. The triiodide complex decomposes as the equilibrium shown in the above equation is displaced to the left by the reduction of the iodine. Such solutions of iodine are not stable. The decrease in oxidizing capacity is not rapid, but the change continues indefinitely. As the rate of change is increased by exposure to light, dark bottles are advisable for the storage of iodine solutions.

Solutions and Standards

As already stated, iodine is dissolved in an aqueous solution of potassium iodide. Although resublimed iodine is sufficiently pure and may be handled as a primary standard,[9] the manipulative details are such that the process usually is not recommended for general work. The atomic weight is the equivalent weight.

When ordinary iodine is used, the solution must be standardized. One of the best methods is to titrate it against N.B.S. arsenious acid [10] according to the reaction

$$(I_2)I^- + AsO_3^{-3} + 2\ HCO_3^- \rightleftarrows AsO_4^{-3} + 3\ I^- + H_2O + 2\ CO_2\uparrow$$

[9] Treadwell-Hall, *op. cit.*, pp. 587-588.

[10] Standard Sample No. 83. Evidence indicates the formula to be As_4O_6, rather than As_2O_3.

Another common method is titration with sodium thiosulfate as a reductant. The reaction

$$2\ S_2O_3^{-2} + (I_2)I^- \rightarrow 3\ I^- + S_4O_6^{-2}$$

is one of the best known in titrimetry. Since the thiosulfate is not itself a primary standard, its solution has to be standardized. Accordingly, the standardization of an iodine solution by titration with standard thiosulfate solution would include the errors involved in two titrations.

The blue coloration produced by iodine and starch is the basis of the most used method of determining the end point in reactions both of iodimetry and thiosulfatimetry, described later. It is considered one of the most sensitive end points in titrimetry. The product obtained from potatoes is considered best. It should be free from partial inversion products, as they may give a pink hue with iodine, and end points in such cases are unsatisfactory.

The indicator compound may be prepared by triturating a 5-g sample of potato starch to a thin paste with 50 ml of water. The paste is poured gradually with stirring, into 5 liters of boiling water. To the cooled solution 5 g of salicylic acid may be added as a preservative. For each 100 ml of solution to be titrated 1 ml of indicator solution should be used.

Applications

The low electrode potential (—0.535 volt) for this oxidant indicates that it does not have the wide oxidizing possibilities of permanganate. The procedure included here is a well-known example. Other applications are illustrated in some of the problems in Chapter 33 and in procedures in reference works.

Exercise 26.9. Preparation of a Standard Solution of Iodine

Calculate the amount of iodine required for 500 ml of 0.1 *N* solution. Weigh this amount approximately on a watch glass and transfer to a large beaker. Add about four times this amount of potassium iodide and then add 300 to 400 ml of water. After stirring to dissolve all soluble material, decant the solution into a 500-ml volumetric flask and dilute to the mark. The solution may be standardized by either of the methods given below. It should be stored in a dark, glass-stoppered bottle to retard the slow reaction between iodine and water which proceeds according to the equation

$$4\ (I_2)I^- + 6\ H_2O \rightarrow 12\ H^+ + 12\ I^- + 3\ O_2\uparrow$$

Standardization Against Arsenious Oxide

Calculate the amount of arsenious oxide of known purity required for 250 ml of 0.1 *N* solution. Weigh this amount of dried material and transfer to a 250-conical flask. Add 100 ml of water and 5 ml of concentrated sulfuric acid. Boil gently to dissolve the oxide. When it is cool, transfer the solution to a 250-ml volumetric flask, dilute to the mark, and mix.

Transfer 50.00 ml of this solution to a liter conical flask and dilute to about 400 ml. Add slowly about 5 g of sodium hydrogen carbonate (*1*). Add 2 ml of starch indicator and titrate with the iodine solution until the blue iodo-starch color persists for 1 min. Calculate the normality of the solution and its titer in terms of arsenic and arsenic trioxide.

NOTE: (1) If the acidity is kept low by means of hydrogen carbonate, the following reaction takes place

$$AsO_3^{-3} + (I_2)I^- + H_2O \rightleftarrows AsO_4^{-3} + 2\ H^+ + 3\ I^-$$

In acidic solutions the reverse reaction takes place. The reaction is an excellent example of the effect of hydrogen ion concentration on the direction of the process. In strongly acidic solutions it is practically complete to the left.

Standardization Against Sodium Thiosulfate

Transfer a 25.00-ml portion of the thiosulfate solution (see page 446) to a conical flask and add 1 ml of starch indicator. Titrate with the iodine solution until the solution is a faint blue from the iodo-starch (*1*). Calculate the normality of the iodine solution and its titer in terms of any constituents for which it is to be used.

NOTE: (1) The titration may be run in the opposite direction, but using the iodine as the titrant avoids the difficulties encountered when the starch is added too soon in going the other way.

Exercise 26.10. Determination of Arsenic in Paris Green

The determination of total arsenic in Paris green provides an example of the use of a standard iodine solution. The commercial product is represented approximately by the formula $Cu_3(AsO_3)_2 \cdot Cu(C_2H_3O_2)_2$. The official distillation method is based upon volatilizing the arsenic as the trichloride, after dissolving the sample in hydrochloric acid and reducing any quinquivalent arsenic to the tervalent state by means of cuprous chloride. After neutralization of the acidic distillate containing the arsenious compound, excess sodium hydrogen carbonate is added and the arsenic titrated to the quinquivalent state with the iodine solution. The reaction is given on page 438.

The method is also applicable, except in the presence of nitrate, to the determination of total arsenic in lead arsenate, calcium arsenate, zinc arsenite, magnesium arsenate, and Bordeaux mixture with arsenicals.

The Sample

Selection and preparation. Mix thoroughly the finely ground material.

Measurement. Weigh on a watch glass a quantity of sample containing not more than 0.4 g of arsenic (*1*) and transfer to a 500-ml distillation flask.

The Desired Constituent

Separation. Add about 5 g of cuprous chloride to the sample and wash all material down into the flask with 100 ml of concentrated hydrochloric acid. Connect the distilling flask to a condenser and arrange these with a burner and receiving flask according to Figure 26.2.

The receiving vessels are 500-ml conical flasks. The first contains 40 ml (*2*) of water and the second 100 ml. Have pieces of ice or running water in the pan to keep the flasks cool.

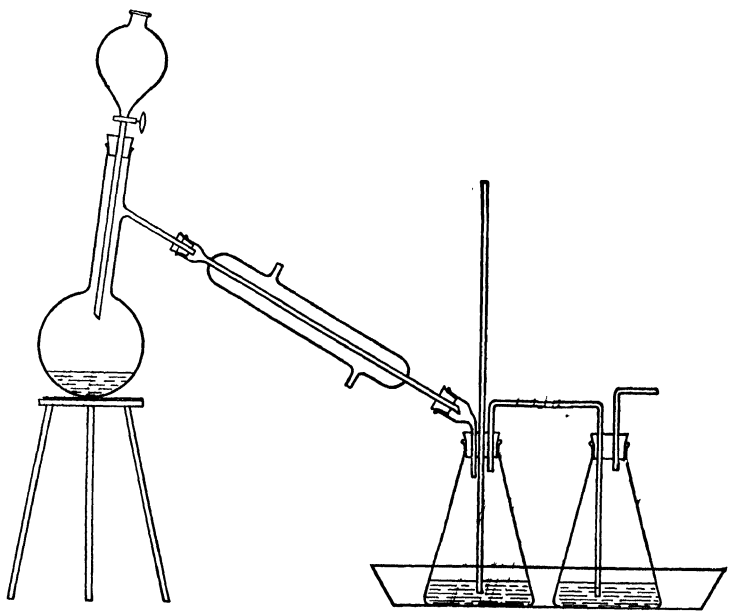


Figure 26.2

Distillation apparatus.

Distill the solution until the volume in the distillation flask is reduced to about 40 ml. Then add 50 ml more acid by means of the dropping funnel and continue the distillation. Repeat this process until about 200 ml of distillate are collected. Rinse off the connecting tubes, transfer the contents of the flasks to a 500-ml volumetric flask, dilute to the mark, and mix.

Measurement. Transfer 100 ml of the solution to a 500-ml conical flask. Nearly neutralize with 10 *M* sodium hydroxide, using two drops of phenolphthalein and keeping the solution cooled (*3*). Add 10 g of finely powered sodium hydrogen carbonate and titrate the solution as directed on page 439. Calculate the percentage of arsenic in the sample (*4*).

NOTES: (1) Theoretically, commercial Paris green may run up to about 25 per cent of arsenic.

(2) Using more than 40 ml may cause the separation of a compound of arsenic that cannot readily be redissolved without loss of arsenious chloride.

(3) Acidify with hydrochloric acid if the solution becomes basic.

(4) To determine copper, treat 2 g of the sample in a beaker with 100 ml of water and about 2 g of sodium hydroxide, and boil thoroughly until all the copper is precipitated as cuprous oxide. Filter, wash well with hot water, dissolve the precipitate in hot nitric acid (1:4), cool, transfer to a 250-ml flask, and dilute to the mark. Determine the copper by the method given under thiosulfatimetry.[11]

CERATIMETRY

Acidic cerate solutions have come into increasing use as standard oxidants.[12] The cerium in these solutions is probably present as a complex anion with the anion of the acid present; e.g., in sulfuric acid solution the species present is probably $Ce(SO_4)_3^{-2}$. The formal oxidation potential of the ceric species will vary with the anion involved, but is generally comparable to that of permanganate ion in acidic solution. For convenience, the cerate species will be represented as the ceric ion Ce^{+4}.

Although the color change of the solution itself is usually not sufficient for indicating the end point of titrations, oxidation-reduction indicators are available which have a redox potential suitable for various reactions. Also the potentiometric method is available for detecting end points. The solution is stable and seems destined to have even more extended use as an oxidant. Typical applications are represented by the following equations:

[11] Assoc. Offic. Agr. Chemists, *Methods of Analysis,* p. 54 (1950).

[12] See Furman, *Neure massanalytische Methoden,* pp. 80-110, Enke, 1951, and *Newer Methods of Volumetric Analysis,* pp. 27-52, Van Nostrand, 1938; Smith, "Cerate Oxidimetry," Smith Chemical Co., 1942; Young, *Anal. Chem.,* **24,** 152 (1952).

$$2\ Ce^{+4} + C_2O_4^{-2} \rightarrow 2\ CO_2\uparrow + 2\ Ce^{+3} + 2\ H^+$$
$$2\ Ce^{+4} + AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2\ Ce^{+3} + 2\ H^+$$
$$2\ Ce^{+4} + H_2O_2 \rightarrow 2\ Ce^{+3} + 2\ H^+ + O_2\uparrow$$
$$Ce^{+4} + Fe^{+2} \rightarrow Ce^{+3} + Fe^{+3}$$

Solutions and Standards

Solutions of trisulfatocerate usually have been prepared from the complex salt $(NH_4)_4Ce(SO_4)_4 \cdot 2\ H_2O$. Since this compound is not a primary standard, the solutions had to be standardized against some material such as sodium oxalate. Smith[13] *et al.* proposed ammonium hexanitratocerate, $(NH_4)_2Ce(NO_3)_6$, as a primary standard. In use its reaction involves dissociation of the complex ion

$$Ce(NO_3)_6^{-2} \rightleftarrows Ce^{+4} + 6\ NO_3^-$$

The electrode reaction, $Ce^{+3} \rightleftarrows Ce^{+4} + 1\ e$, shows that the molecular weight of either complex salt is the equivalent weight.

Applications

A variety of determinations involving the use of the cerate ion as the standard oxidant are included in the references already mentioned. Thus, any of the determinations given under permanganimetry may be performed ceratimetrically.

As a specific example, the determination of oxalic acid or of iron is suggested. The sample of oxalic acid is handled as under permanganimetry and its measurement is made in the same manner as the standardization of the cerate solution against sodium oxalate. To determine iron in an ore, follow the directions given under dichromatimetry to the point of titrating the reduced solution. Then continue the determination as described there, except for the use of cerate instead of dichromate as the titrant.

Exercise 26.11. Preparation of a Standard Cerate Solution

Ammonium hexanitratocerate is the most suitable compound for preparing the solution as it is a primary standard. Smith *et al.* have given details[13] for its preparation from commercial ceric oxide. Its molecular weight is 548.26.

Hydrated ceric oxide $CeO_2 \cdot 2\ H_2O$, ceric sulfate $Ce(SO_4)_2 \cdot 4\ H_2O$, and ammonium sulfatocerate $(NH_4)_4Ce(SO_4)_4 \cdot 2\ H_2O$, are the common materials from which to prepare a solution that has to be standardized. Directions are given below for the preparation of a solution from either the nitrate or the sulfate.

[13] Smith *et al.*, *Ind. Eng. Chem., Anal. Ed.*, 8, 449 (1936).

Procedure

(a) Weigh 54.83 g of primary-standard-grade ammonium hexanitratocerate and transfer to a liter flask. Dissolve in 0.5 *M* sulfuric acid, dilute to the mark, and mix. The solution will be 0.1000 *N* (*1*).

(b) Dissolve 80 g of ceric ammonium sulfate (*2*) in a liter flask with 500 ml of water containing 28 ml of concentrated sulfuric acid. Dilute to the mark with water and mix.

This solution must be standardized against some primary standard such as arsenious oxide or sodium oxalate

$$2\ Ce^{+4} + AsO_3^{-3} + H_2O \rightarrow AsO_4^{-3} + 2\ Ce^{+3} + 2\ H^+$$
$$2\ Ce^{+4} + C_2O_4^{-2} \rightarrow 2\ CO_2\uparrow + 2\ Ce^{+3}$$

The oxalate standardization is given here.

Calculate the amount of sodium oxalate required for 35 ml of 0.1 *N* ceric sulfate solution. Weigh this amount of oxalate, transfer to a 250-ml beaker, and dissolve in about 100 ml of water. Add 15 ml of concentrated hydrochloric acid and 5 ml of 0.005 *M* iodine monochloride (*3*). Heat the solution to 50°, add a drop of 1,10-phenanthroline-ferrous complex indicator (*4*) and titrate with the ceric solution to a faint blue hue which persists for at least a minute. It may be found preferable to take the disappearance of the red hue as an end point. Calculate the normality of the solution.

NOTES: (1) If for any reason the nitrate ion is objectionable, it may be removed by evaporating a known weight of the nitrate salt with excess sulfuric acid.

(2) An average purity of 80 per cent is assumed for the usual commercial material.

(3) To prepare a solution of the catalyst iodine monochloride, dissolve 0.279 g of potassium iodide and 0.178 g of potassium iodate in 250 ml of water and add 250 ml of concentrated hydrochloric acid. The rate of oxidation is too slow without this catalyst.

(4) The indicator is prepared by dissolving the calculated amount of 1,10-phenanthroline, $C_{12}H_8N_2 \cdot H_2O$, in 0.025 *M* solution of ferrous sulfate.

(5) The temperature should not fall below 45°.

OTHER OXIDIZING SOLUTIONS

In addition to the oxidants already discussed, three others worthy of mention here are potassium iodate, potassium bromate, and sodium chlorite. Included below are only references to sources of information regarding the application of solutions of these compounds for accomplishing oxidations, together with several equations to illustrate the use of each.

Iodatimetry

Lang, *Neure massanalytische Methoden,* pp. 121-179, 1951, and *Newer Methods of Volumetric Analysis,* pp. 69-128, Van Nostrand, 1938; Treadwell-Hall, *Analytical Chemistry,* Vol. II, pp. 623-628, Wiley, 1942.

$$4\ CuSCN + 7\ KIO_3 + 14\ HCl \rightarrow 4\ HCN + 4\ CuSO_4 + 7\ ICl + 7\ KCl + 5\ H_2O$$

$$KIO_3 + 2\ H_2SnCl_4 + 6\ HCl \rightarrow 2\ H_2SnCl_6 + KCl + ICl + 3\ H_2O$$

$$KIO_3 + 2\ SO_2 + 2\ HCl + H_2O \rightarrow KCl + ICl + 2\ H_2SO_4$$

$$KIO_3 + 8\ KI + 6\ HCl \rightarrow 3\ K(I_2)I + 6\ KCl + 3\ H_2O$$

Bromatimetry

Lang, *Neure massanalytische Methoden,* pp. 121-179, Enke, 1951; Treadwell-Hall, *Analytical Chemistry,* Vol. II, pp. 628-635, Wiley, 1942.

$$KBrO_3 + 3\ Na_3AsO_3 + (HCl) \rightarrow KBr + 3\ Na_3AsO_4$$

$$KBrO_3 + 5KBr + 6\ HCl \rightarrow 6\ KCl + 3\ H_2O + 3\ Br_2$$

$$KBrO_3 + 3\ SbCl_3 + 6\ HCl \rightarrow 3\ SbCl_5 + KBr + 3\ H_2O$$

Chloritimetry

Kolthoff and Stenger[14] proposed calcium hypochlorite as a standard oxidizing agent, and Jackson and Parsons suggested[15] sodium chlorite for similar work. Details may be found in the original sources.

Reductimetry

As the complement of oxidimetry, reductimetry includes the use of standard solutions of reductants for the measurement of oxidizing substances. At least two factors combine to make such methods less useful than those of oxidimetry for direct titrations. Most reductants are instable unless they are maintained in an oxygen-free environment, and the potentiometric method may be the only feasible procedure for locating the end point. In the latter case, one may resort to the frequently used process of back-titration of an excess of reductant with a standard solution of an oxidant. The reductants sodium oxalate and arsenious oxide have been used as primary standards.

Typical applications of several common reductants are given below.

THIOSULFATIMETRY

One of the most useful reductants is the thiosulfate ion.[16] Although it might be considered as a general reductant, its use is confined to the

[14] *Ind. Eng. Chem., Anal. Ed.* **7**, 79 (1935).
[15] *Ind. Eng. Chem., Anal. Ed.* **9**, 14 (1937).
[16] Treadwell-Hall, *op. cit.,* pp. 583-623.

titration of iodine, according to the reaction

$$(I_2)I^- + 2\ S_2O_3^{-2} \rightarrow 3\ I^- + S_4O_6^{-2}$$

This process may be for the purpose of determining the iodine itself. Generally, however, it is only incidental to the measurement of other constituents. Through an appropriate reaction, the desired constituent liberates an equivalent amount of iodine which may then be titrated.

Solutions and Standards

The reagent commonly employed is sodium thiosulfate, $Na_2S_2O_3 \cdot 5\ H_2O$, the equivalent weight being the molecular weight.

The uncertainty in the degree of hydration makes direct weighing impractical.[17] If the solution is to be used for general work, one of the most convenient methods of standardization is to employ potassium dichromate of known purity. An acidified solution of this salt reacts with an excess of potassium iodide to liberate an equivalent amount of triiodide ion according to the reaction

$$Cr_2O_7^{-2} + 9\ I^- + 14\ H^+ \rightarrow 2\ Cr^{+3} + 7\ H_2O + 3\ (I_2)I^-$$

The triiodide is then titrated with the thiosulfate. A standard solution of potassium dichromate, prepared by direct weighing, will serve. If a standard solution of potassium permanganate is at hand, it may be used in place of the dichromate, although it is a secondary standardization. Similarly, an "iodine" solution may be used, after standardization according to the procedure already described.

It may be desirable, or even necessary, to standardize the solution under conditions comparable to those encountered in its use. The reductimetric determination of copper, described later, is an example. In this case a sample of commercial copper, which is obtainable in a high degree of purity, is carried through the same process as the unknown.

There has been much discussion regarding the possible factors affecting the stability of solutions of thiosulfate. It has been reported by some individuals to be stable for several months if boiled water is used in its preparation. This process probably eliminates sulfur-liberating bacteria from the system and also reduces the acidity owing to dissolved carbon dioxide. Reactions such as those expressed by the following equations have been stated to take place in slightly acidic solutions

$$Na_2S_2O_3 + 2\ HCl \rightarrow 2\ NaCl + H_2S_2O_3$$
$$H_2S_2O_3 \rightarrow H_2SO_3 + S$$

[17] The anhydrous salt has been recommended as a primary standard. See Tomlinson and Ciapetta, *Ind. Eng. Chem., Anal. Ed.* **13**, 539 (1941).

In such solutions an opalescence, usually attributed to the presence of colloidal sulfur, is often developed. Addition of a minute amount of sodium carbonate to keep the solution slightly alkaline seems to increase stability.

Applications

Of the large number of methods available in thiosulfatimetry only two have been selected: the determination of copper in an ore and of manganese in pyrolusite. Others may be found in reference works.

Exercise 26.12. Preparation of a Standard Solution of Sodium Thiosulfate

Calculate the amount of sodium thiosulfate, $Na_2S_2O_3 \cdot 5\ H_2O$, required for 1 liter of 0.1 *N* solution. Since the composition of the salt is not sufficiently certain to warrant direct weighing, only an approximate amount need be taken. Dissolve the salt in boiled, cooled water, add 0.2 g of sodium carbonate, dilute to 1 liter, and mix. Standardize the solution by one of the two methods given below.

Standardization Against Potassium Dichromate

Prepare 250 ml of 0.1000 *N* potassium dichromate solution (*1*). Transfer 25.00 ml of this solution to a 500-ml conical flask and add to it about 6 g of potassium iodide (*2*). Acidify the solution with 10 ml of concentrated hydrochloric acid. Dilute to about 200 ml and after 3 min., titrate the liberated iodine with the thiosulfate solution. When the iodine color (*3*) has nearly disappeared (*4*), add about 2 ml of starch indicator solution and continue the titration until the blue iodo-starch hue just disappears (*5*).

Run a blank on the potassium iodide solution (*6*) by using the same amount and running it through the same way except for the omission of the dichromate solution.

After making correction for any blank obtained, calculate the normality of the thiosulfate and its titers in terms of any constituents that are to be determined on the basis of this standardization (*7*).

NOTES: (1) Any standard solution of potassium dichromate available may be used, or separate portions of the salt may be weighed. How many milliliters of 0.1 *N* sodium thiosulfate are equivalent to 25 ml of dichromate solution having a titer of 0.005000 g in terms of iron?

(2) There must be an excess of potassium iodide. Why?

(3) As the titration proceeds, the coloration from the liberated iodine decreases but the hue of the tervalent chromium persists.

(4) If the starch is added too soon, it is difficult to obtain a satisfactory end point, owing to the formation of an iodo-starch precipitate.

(5) The solution should be a clear, emerald green at this point. Standardization against potassium bromate avoids the color encountered with tervalent chromium.

(6) Any iodates in the solution will liberate iodine according to the reaction

$$IO_3^- + 6\ H^+ + 5\ I^- \rightarrow 2\ (I_2)I^- + 3\ H_2O$$

This necessitates running a blank determination under the conditions of the experiment.

(7) Amyl alcohol in the proportion of 5 ml per liter of solution has been recommended as a preservative for the thiosulfate solution. Some analysts prefer chloroform (5 ml) or a 0.1 per cent solution of sodium furoate.

Standardization Against Metallic Copper

Dissolve separate weighed pieces of about 0.2 g of copper wire (*1*) of known purity (*2*) in a 250-ml conical flask by warming with 5 ml of nitric acid (1:1). Add about 25 ml of water and boil 1 min. to expel oxides of nitrogen (*3*). Slowly add about 0.5 g of urea and boil for 1 min. (*4*). Cool and buffer the solution by adding 6 *M* ammonium hydroxide slowly and with swirling until the color of the deep-blue complex persists, or until a pale-blue precipitate of cupric hydroxide persists (*5*). Acidify with 6 *M* acetic acid and add 5 ml in excess. *From this point on, complete each sample before starting another.*

Add about 3 g of potassium iodide, allow to stand 2 min., and then titrate immediately the liberated iodine with thiosulfate solution until the brownish hue is nearly gone (*6*). Add 2 ml of starch indicator solution and about 2 g of ammonium thiocyanate (*7*), shake well, and continue the titration until only the white color of the cuprous iodide (some cuprous thiocyanate) is visible. Since a pure white is seldom obtained, take as the end point the last drop that causes a perceptible change in hue.

After making any necessary correction for iodates in the potassium iodide used (*8*), calculate the titer of the solution in terms of copper.

NOTES: (1) How much copper is equivalent to 25 ml of 0.1 *N* sodium thiosulfate?

(2) The purity is easily determinable by the electrodeposition-gravimetric process (see page 491).

(3) Dissolution of the copper involves the following reactions

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 4\ H_2O + 2\ NO$$
$$2\ NO + O_2 \rightarrow 2\ NO_2$$
$$NO + NO_2 + H_2O \rightarrow 2\ HNO_2$$

The nitrous acid would oxidize hydriodic acid.

(4) Urea will reduce any remaining nitrous acid.

(5) Too much ammonium hydroxide produces later so much ammonium acetate that the reaction of the cupric ion with the iodide ion is incomplete, as indicated by

the fact that the solution remains blue. If excess ammonia is added, boil the solution until cupric hydroxide begins to precipitate.

(6) The cuprous iodide precipitate obscures the end point somewhat.

(7) The ammonium thiocyanate apparently releases the iodine adsorbed on the cuprous iodide, through the formation of the less soluble cuprous thiocyanate [see Foote, *J. Am. Chem. Soc.* **60,** 1349 (1938)].

(8) The correction is obtained by making a determination without any copper present.

Exercise 26.13. Determination of Copper in an Ore

The reductimetric method for determining copper is based upon the fact that cupric ion reacts, at a suitable *p*H, with an excess of iodide ion according to the reaction

$$2\ Cu^{+2} + 5\ I^- \rightarrow 2\ CuI\downarrow + (I_2)I^-$$

precipitating cuprous iodide and liberating an equivalent amount of triiodide ion. This product can then be titrated with thiosulfate, according to the equation

$$(I_2)I^- + 2\ S_2O_3^{-2} \rightarrow 3\ I^- + S_4O_6^{-2}$$

Some materials, such as certain ores, contain other metals that form insoluble iodides or the salts of which oxidize iodides and thus interfere with the determination. In such cases it is necessary to remove these constitutents or to convert them to inert forms. Park's method,[18] given here, is considered an improvement over the older method in which the copper is separated by electrochemical displacement. The procedure given is for an ore.

The Sample

Selection and preparation. Select representative portions; mix and grind them until the material passes a 100-mesh screen.

Measurement. Weigh on a watch glass about 0.5 g of the dried material and transfer to a casserole (*1*).

Treatment. To the covered casserole add 10 ml of concentrated hydrochloric acid and heat slowly. If the copper is not dissolved in 10 min., add 5 ml of concentrated nitric acid and continue the heating (*2*).

If nitric acid has been used, add 5 ml of concentrated sulfuric acid, raise the cover glass on hooks, and evaporate (hood) the solution until dense white fumes of sulfur trioxide appear (*3*). Preliminary evaporation may be done on the steam bath. Finally, hold the casserole in the hand over a low flame (*4*) and keep the contents swirling constantly.

[18] Park, *Ind. Eng. Chem., Anal. Ed.* **3,** 77 (1931).

After obtaining the sulfur trioxide vapor, allow the casserole to cool. Add 20 ml of water, 5 ml of bromine water (*5*), and boil for 3 to 5 min. to expel excess bromine (*6*).

Cool the solution and add just enough 6 *M* ammonium hydroxide to produce a slight permanent precipitate of hydrous ferric oxide, if any iron is present, or until the deep-blue complex of copper persists. Then add 5 ml of glacial acetic acid (*7*). Transfer the solution to an old beaker (*8*) and add 1 to 2 g of ammonium fluoride (*9*).

The Desired Constituent

Measurement. Dissolve about 3 g of potassium iodide in the solution and titrate at once with thiosulfate according to the directions for standardizing the titrant. Calculate the percentage of copper.

NOTES: (1) For alloy samples take 0.2 to 0.4 g samples and dissolve in 10 ml of 1:1 nitric acid.

(2) If a globule of sulfur appears that is dark on cooling, remove and wash it. Ignite in a porcelain crucible, dissolve the residue in nitric acid and add to the original solution.

(3) Any nitric acid remaining may oxidize some iodide ion.

(4) It is more convenient to suspend an infrared evaporating lamp about 5 mm above the edge of the casserole.

(5) Bromine oxidizes any arsenic and antimony to the quinquivalent state and iron to the tervalent state.

(6) Excess bromine oxidizes the iodide ion.

(7) The *p*H should be near 3.8.

(8) Etching of the beaker will prevent its acceptance at the store room.

(9) The fluoride ion prevents interference of iron through formation of the fluoferrate ion FeF_6^{-3}. Ferric ion will oxidize the iodide ion.

Exercise 26.14. Determination of Manganese in Pyrolusite

Certain uses of manganese dioxide rest on its capacity as an oxidizing agent, as measured by its capacity to liberate chlorine from a solution of hydrochloric acid. This is expressed sometimes in terms of available oxygen. The chlorine evolved is passed into a solution of potassium iodide where it liberates an equivalent amount of iodine which may then be titrated. The following reactions are involved

$$MnO_2 + 4\ HCl \rightarrow MnCl_2 + 2\ H_2O + Cl_2\uparrow$$
$$3\ I^- + Cl_2 \rightarrow 2\ Cl^- + (I_2)I^-$$
$$(I_2)I^- + 2\ S_2O_3^{-2} \rightarrow 3\ I^- + S_4O_6^{-2}$$

Some peroxides react similarly. In some cases it is not necessary to separate the chlorine by volatilization.

The Sample

Selection and preparation. Select suitable representative material and grind it to 100-mesh size.

Measurement. Weigh 0.3 g of dried material on a watch glass and transfer to the evolution flask of a Bunsen chlorine apparatus (Figure 26.3).

The Desired Constituent

Separation. Transfer 30 ml of a solution of potassium iodide containing 125 g per liter to the receiving flask of the Bunsen apparatus and dilute with 25 ml of water (*1*). Connect the receiving end of the delivery tube to the evolution flask and secure the whole apparatus so that the other end dips below the surface of the potassium iodide solution, as shown in Figure 26.3. The receiving flask should be partially immersed in ice water (*2*).

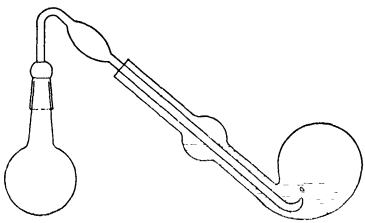


Figure 26.3

Bunsen distillation apparatus.

Add 30 ml of concentrated hydrochloric acid to the evolution flask and connect the delivery tube at once. Heat the flask slowly but steadily (*3*) to volatilize the chlorine into the receiving flask (*4*). Raise the temperature to boiling, and continue for 5 min. after visible action ceases. Raise the end of the delivery tube above the surface of the solution and then remove the burner. Rinse off the tube into the receiving flask.

Measurement. Wash the potassium iodide solution out of the receiving flask into a conical flask and titrate at once with thiosulfate until the color almost disappears. Add 1 ml of starch indicator and continue the titration to the disappearance of the blue hue.

Calculate the results in terms of manganese (*5*), or of the oxidizing capacity of the pyrolusite.

NOTES: (1) There should be enough solution to seal the bend in the receiving flask when the latter is inclined.

(2) The low temperature helps to prevent the loss of chlorine and iodine.

(3) Once heating has started, any lowering of the temperature in the evolution flask, either through lowering the flame or having it blown aside, is likely to ruin the determination by causing the potassium iodide solution to be sucked back into the evolution flask.

(4) As soon as any chlorine reaches the potassium iodide solution, the latter begins to turn dark from the liberated iodine.

(5) Manganese is really not measured directly.

FERROIMETRY

Methods of ferroimetry include those in which the ferrous ion functions as the titrant. The solution used is usually one of either ferrous or ferrous ammonium sulfate. Such systems, in contact with air, are slowly oxidized. Increased stability is achieved by acidifying with sulfuric acid. Some analysts keep a strip of sheet aluminum in the solution to prevent oxidation. Occasional restandardization is recommended.

Solutions and Standards

Either ferrous sulfate, $FeSO_4 \cdot 7\,H_2O$, or ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$, may be used. The degree of hydration of the double salt is somewhat more certain. At times it has been specified as a primary standard, but the National Bureau of Standards does not recognize it as such. In either case, the equivalent weight is the molecular weight. Standardization should be made against a suitable oxidant, such as permanganate or dichromate.

Applications

The general use of standard ferrous ion solutions in measurement involves the back titration with a standard oxidant solution of the excess standard ferrous solution added to the oxidant being determined. In the method already given for chromium, the excess ferrous solution is titrated with dichromate. The discovery of more suitable oxidation-reduction indicators will undoubtedly extend the use of reductants for direct titrations. One such application of the ferrous solution is given below.

Exercise 26.15. Determination of Chromium

In the method of determining chromium by direct titration the sample is carried through the same steps as in the back titration method up to the point of titration, page 432. At that point three drops of diphenylbenzidine indicator (1 g/100 ml of concentrated sulfuric acid) is added to the cold solution and the titration is made with a standard solution of ferrous sulfate. The end point is taken at the change from purple to green.

ARSENIOMETRY

Arsenic trioxide, one of the few primary standards supplied by the National Bureau of Standards for titrimetric work, is of use for checking certain oxidants and also for preparing a standard solution of sodium

arsenite for use in general reductimetric work. Although it is generally used for back titrations, an important direct titration in which it is used is the determination of manganese in steel. After oxidizing the manganese to permanganate, the latter is titrated with arsenite solution.[19]

OTHER REDUCTANTS

Various other compounds can be used as reductants. Titanous chloride is a vigorous reactant and has important applications.[20] It is so easily oxidized that great care must be taken to protect the solution from oxidation by the air.

Sodium oxalate is important as a primary standard for checking oxidants. Oxalic acid has some use in back titrations. Hydrogen peroxide is used in the same way occasionally, as is chlorostannous acid.

[19] Lundell, Hoffman, and Bright, *Chemical Analysis of Iron and Steel,* p. 195, Wiley, 1931.
[20] Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis,* Longmans, 1918.

CHAPTER 27

PRECIPITATION AND COMPLEXATION METHODS[1]

Solutions and Standards

In the group of methods based on insolubility, or on slight dissociation of a reaction product other than water, no one standard solution is used for a large number of different determinations, as is the case with certain neutralizing, reducing, and oxidizing solutions. The most widely used standard solutions are those of silver, mercuric, thiocyanate, cyanide, and ferrocyanide [hexacyanoferrate (II)] ions.

The most commonly used primary standards are probably sodium and potassium chlorides, and silver nitrate. Many of the solutions used in precipitation and complexation reactions are standardized against a known sample of the substances to be determined.

Some writers use the terms argentimetry, thiocyanatimetry, and ferrocyanidimetry in referring, respectively, to applications of solutions of silver, thiocyanate, and ferrocyanide ions as titrants.

Applications

A number of standard solutions of this nature are used for only a single kind of determination, for example, thiocyanate ion for silver and barium ion for sulfate. Some solutions, such as mercuric nitrate, are used almost exclusively in complexation reactions, whereas others, such as potassium cyanide, are used in titrations involving either precipitation or complex-formation.

Exercise 27.1. Preparation of a Standard Solution of Silver Nitrate

Although the practice of weighing silver nitrate directly is not usually considered the best on account of some uncertainty regarding its purity,

[1] See Chapters 12 and 15 for a discussion of this subject.

this procedure may be followed if certified reagent material is used and the requirements of accuracy are not too exacting. If necessary for the work to be done, the solution may be standardized by one of the methods suggested below.

Direct Weighing

Calculate the amount of silver nitrate required for 500 ml of a solution either 0.1 *N* or having a definite titer in terms of chlorine (*1*). Weigh the salt on a watch glass, transfer to a 500-ml flask, dissolve in water (*2*), and dilute to the mark. Keep the solution out of strong light (*3*).

Standardization Against Sodium Chloride

Prepare the solution as directed above. Weigh out separate portions of pure, dry (*4*) sodium chloride (*5*), each equivalent to 25 to 35 ml of of the silver nitrate solution. Dissolve in about 50 ml of water and titrate with the solution to be standardized by one of the procedures given below for the determination of chloride ion (*6*).

NOTES: (1) How much silver nitrate, 99.8 per cent pure, is required for 500 ml of a solution, each milliliter of which is equivalent to 0.005000 g of chlorine?

(2) Add three drops of concentrated nitric acid per liter to prevent the formation of deposits.

(3) If the solution is to be kept long, it should be preserved in an amber-colored bottle.

(4) Complete removal of all water requires heating at about 600°, a temperature attained best in an automatically controlled electric furnace.

If the standard sodium chloride used in connection with the instructor's analysis of the samples was dried at 110°, this same temperature should be used by the student for the same samples.

(5) Some analysts prefer potassium chloride.

(6) A measured portion of the solution may be standardized gravimetrically by separating the silver as such by electrodeposition, or by separating it by precipitation in the form of silver chloride, as described in Chapter 28.

Exercise 27.3. Preparation of a Standard Solution of Potassium Thiocyanate

Potassium (or ammonium) thiocyanate is usually used to react with silver nitrate, either to determine silver or to back-titrate an excess of a standard solution of silver.

Procedure

Calculate the amount of potassium (or ammonium) thiocyanate required for 1 liter of a solution either 0.1 *M* or having a silver titer of 0.005000 g. Weigh out about 2 per cent more than this amount if the

solution is to be adjusted to a definite value (*1*). Dissolve in water and dilute to the mark.

To standardize the solution, transfer 25.00 ml of the standard silver nitrate solution to a conical flask, together with about 40 ml of water. Add 1 ml of ferric alum indicator solution (*2*), and titrate with the thiocyanate until the red hue of the ferric-thiocyanate complex just appears. Calculate the normality of the solution, or its titer in terms of silver (*3*).

NOTES: (1) If potassium thiocyanate is carefully prepared, it may be weighed as a primary standard [Kolthoff and Lingane, *J. Am. Chem. Soc.* **57**, 2126 (1935)].

(2) The indicator is a solution of ferric ammonium sulfate, saturated at room temperature, to which has been added enough nitric acid to prevent hydrolysis and give a clear, pale-yellow hue.

(3) If an exact value is desired, calculation of the water per liter to add must be made at this point.

Exercise 27.3. Determination of Silver Ion

The Volhard method for determining silver is based upon the reaction

$$Ag^+ + SCN^- \rightarrow AgSCN \downarrow$$

In the presence of ferric alum as an indicator the first excess of titrant produces a soluble red complex, long thought to be $Fe(SCN)_3$. Present evidence seems to indicate that the composition of the complex depends upon the ratio of the ferric to the thiocyanate ions. Initially, the reaction at low ratio of thiocyanate to iron concentration is probably

$$Fe^{+3} + SCN^- \rightarrow FeSCN^{+2}$$

As more SCN^- ion is added, the next product formed is $Fe(SCN)_2^+$ with the final product of the series of such stepwise additions being $Fe(SCN)_6^{-3}$.

The Sample

Selection. Select suitable samples of alloy or other material (*1*).

Measurement. Weigh about 0.25 g of the material and transfer to a 250-ml conical flask.

Treatment. Dissolve in 10 ml of 1:1 nitric acid and boil out the oxides of nitrogen. Cool, and add about 60 ml of water.

The Desired Constituent

Measurement. Titrate with thiocyanate solution according to the method used above in its standardization. Calculate the percentage of silver.

NOTE: (1) Mercury, nickel, and cobalt should be absent. The first forms an insoluble thiocyanate, and the color of the other two interferes if there is much present. Not more than 60 per cent of the sample should be copper.

Exercise 27.4. Determination of Chloride Ion

The frequently encountered problem of determining chlorine in the form of chloride ion is generally accomplished by means of a standard solution of silver nitrate. The determination is made either by a direct titration or by adding an excess of silver nitrate and back-titrating with thiocyanate. Directions are given below for applying the direct titration in the presence of either potassium chromate (Mohr method) or dichlorofluorescein (Fajans method) as internal indicators, and also for the back-titration procedure (Volhard method).

The Sample

Selection and Preparation. Select a representative sample of the halide to be analyzed and grind it well (*1*).

Measurement. Weigh out about 0.25 g of the sample. Transfer to a 250-ml casserole if the Mohr method is to be used. Use a 250-ml beaker for the Volhard method, and a 250-ml conical flask for the Fajans method.

Treatment. Dissolve the sample in about 25 ml of water.

The Desired Constituent

Measurement. Procedure A (Volhard). Acidify the solution with nitric acid and then add 50.00 ml of the standard solution of silver nitrate. Digest the precipitate 15 min. on the hot plate, filter (*2*) on paper and wash the silver chloride thoroughly with hot water (*3*). Titrate the excess silver nitrate in the filtrate with the thiocyanate solution, according to the Volhard method already described for silver. Calculate the percentage of chloride.

NOTES: (1) The method is applicable also to bromides and iodides.

(2) Removal of the precipitated silver chloride prevents its reaction with added thiocyanate

$$AgCl + SCN^- \rightarrow AgSCN + Cl^-$$

since the solubility of the silver thiocyanate is less than that of silver chloride.

(3) Caldwell and Moyer [*Ind. Eng. Chem., Anal. Ed.* **7**, 38 (1935)] recommend adding 1 to 3 ml of nitrobenzene and omitting the filtration.

Procedure B (Mohr). Make the solution just acidic with nitric acid, nearly neutralize with sodium hydroxide, and then add small amounts of

solid calcium carbonate until a slight excess remains undissolved (*1*). To the solution in a white dish or casserole (*2*) add six drops of *M* potassium chromate indicator solution (*3*) and titrate until the solution in the casserole becomes perceptibly red from silver chromate. Restore the yellow hue by adding a few drops of a solution of sodium chloride and set the system aside for comparison purposes. Now repeat the procedure, titrating until the solution assumes a definitely brownish-red hue when compared with the undertitrated mixture first prepared. Calculate the percentage of chloride.

NOTES: (1) Appreciable acidity prevents the formation of red silver chromate, which indicates the end point. Basic solutions precipitate silver oxide. Calcium carbonate neutralizes excess acid.

(2) A white dish as a background aids in detection of the end point.

(3) In preparing the indicator add just enough silver nitrate to give a red precipitate. Filter off the precipitated chromate and use the clear solution.

Procedure C (*Fajans*). Add about 40 ml of water and acidify by adding dilute nitric acid dropwise until the solution is just acidic to litmus paper (*1*). Add solid calcium carbonate until an excess remains undissolved (*2*). Add ten drops of dichlorofluorescein indicator (*3*) and 0.1 g of dextrin (*4*). Titrate with standard silver nitrate until the suspended silver chloride changes from a yellowish-white to the hue of a strawberry milkshake (*5*). If less than 20 ml of titrant is required, consider the first titration as a preliminary exercise and adjust the sample weight accordingly (*6*). Calculate the percentage of chloride.

NOTES: (1) Disregard any insoluble residue not affected by the acid.

(2) Calcium carbonate neutralizes excess acid.

(3) The dichlorofluorescein solution contains 0.1 g of solid per 100 ml of 60 per cent ethanol.

(4) Dextrin acts as a protective colloid to prevent the coagulation of the silver chloride.

(5) Diffuse daylight is required, since end points are difficult to detect in direct sunlight or artificial light from plain tungsten-filament bulbs. Strong sunlight darkens the precipitate.

(6) Do not use samples of more than 1 g.

Exercise 27.5. Preparation of a Standard Solution of Potassium Ferrocyanide

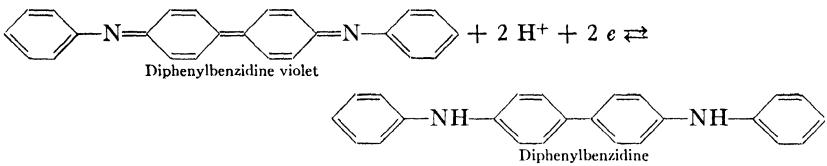
When potassium ferrocyanide is used for titrating zinc ion, the reaction is assumed to be

$$3\ Zn^{+2} + 2\ K_4Fe(CN)_6 \rightarrow K_2Zn_3[Fe(CN)_6]_2 \downarrow + 6\ K^+$$

This relation of zinc to ferrocyanide must be kept in mind when preparing a solution having a given normality or zinc titer.

For many years the uranyl or molybdate ion was used as an outside indicator. At the present time certain oxidation-reduction internal indicators are recommended, perhaps the best being diphenylbenzidine.

Although a solution of ferrocyanide is a precipitating titrant for zinc ions, detection of the end point with diphenylbenzidine involves an oxidation-reduction phenomenon. In the use of this indicator a little ferricyanide, $Fe(CN)_6^{-3}$, is first added to produce the violet oxidized form, diphenylbenzidine violet. Colorless diphenylbenzidine is formed by reduction with the first excess of ferrocyanide titrant. The indicator equilibrium reaction is said to be



The diphenylbenzidine is first formed by oxidation of the diphenylamine.

In actual practice the recommendation is to overtitrate slightly with ferrocyanide and then backtitrate with a standard zinc solution.

Procedure

Calculate the weight of potassium ferrocyanide, $K_4Fe(CN)_6 \cdot 3H_2O$, for 500 ml of 0.05 *M* solution. Prepare the solution and add 0.1 g of sodium carbonate to aid in stabilizing the system.

Prepare 500 ml of a 0.05000 *M* solution of zinc by weighing analytical-grade zinc. Dissolve in a beaker with 500 ml of sulfuric acid (1:10), transfer the solution to a 500-ml volumetric flask, dilute to the mark, and mix.

Standardize the ferrocyanide solution by method (a) or (b) below.

a. Inside indicator. Transfer 25.00 ml of the zinc solution to a 250-ml conical flask. Add 50 ml of water, 20 ml of 6 *N* sulfuric acid, and 2 g of ammonium sulfate. Next, add two drops each of 1 per cent solutions of potassium ferricyanide (*1*) and diphenylamine indicator (*2*).

After development of a blue hue, titrate with ferrocyanide solution until about 1 ml is added beyond the point where this blue is transformed to a greenish tint. The excess ferrocyanide is determined by backtitration to a blue-violet hue with the standard zinc solution.

For the best results, determine the indicator blank by running another determination, without zinc, under the same conditions.

b. Outside indicator. Transfer 25.00 ml of the zinc solution to a 500-ml beaker. Add 20 ml of 6 *N* sulfuric acid and 200 ml of water. After heating almost to boiling, titrate with the ferrocyanide solution. At intervals (*3*) transfer a drop of the solution being titrated to a test plate containing, as an outside indicator, drops either of a solution nearly saturated with uranyl acetate or of a solution 2 per cent in ammonium molybdate. The end point is marked by the appearance of a yellow or brown precipitate. Several minutes are required after mixing on the test plate to develop the precipitate.

Calculate the molarity of the solution or its zinc titer.

NOTES: (1) Dissolve 1 g of $K_3Fe(CN)_6$ in 100 ml of water.

(2) Dissolve 1 g of diphenylbenzidine in 100 ml of concentrated sulfuric acid.

(3) Removal of much solution for testing reduces the accuracy of the determination. One method of decreasing the error is to start with five samples. In the first, test for the end point after addition of each 5 ml of titrant. In the second, test at each ml within the 5-ml interval where the end point lies. In the third, test at each 0.1 ml within the 1-ml interval where the end point lies. The fourth and fifth can be used for final checks then on the titrant.

Exercise 27.6. Determination of Zinc in an Ore

This titrimetric determination of zinc is usually made by means of potassium ferrocyanide, following the method just described for standardizing a ferrocyanide solution. When the unknown sample is an ore, the longest part of the determination is the separation of the zinc from interfering constituents. The method given represents a combination of separations by precipitation and electro-displacement.

The Sample

Selection and preparation. Select and grind representative portions of the sample to be analyzed.

Measurement. Weigh 0.5 g samples (*1*) and transfer to 250-ml casseroles.

Treatment. Add 5 ml each of concentrated hydrochloric and nitric acids. Warm to decompose the ore and then boil out the brown oxides of nitrogen. Remove the cover glass, cool, and add 5 ml of concentrated sulfuric acid. Evaporate until the white fumes of sulfur trioxide appear, swirling the solution while holding the casserole in the hand, or using an infrared evaporating lamp above the surface. After cooling, add about 50 ml of water and warm to dissolve all soluble material.

The Desired Constituent

Separation. Place in the solution a sheet of heavy gauge aluminum, 2 x 15 cm, bent into circular form. Boiling for 10 min. should remove all hue except a little green from ferrous sulfate (*2*). Pour the solution over a piece of aluminum in a filter, catching the filtrate in a 500-ml conical flask, also containing a strip of aluminum. Wash with hot water.

Neutralize the solution with a 10 per cent solution of sodium hydrogen carbonate, using methyl orange indicator. Make just acidic with 20 per cent formic acid and then add five drops in excess (*3*). Dilute to 200 ml and add 4 g of ammonium thiocyanate (*4*). Heat the solution to boiling and pass a stream of hydrogen sulfide through it by means of a tube passing through a rubber stopper. After most of the zinc has precipitated from the boiling solution, insert the stopper to increase the pressure.

When the precipitate coagulates well, filter the solution through a paper and wash the precipitate with hot water (*5*). Put the precipitate (with the paper) back into the flask and add 10 ml of concentrated hydrochloric acid, together with 90 ml of water. Warm to dissolve the precipitate (*6*) and boil out hydrogen sulfide.

Measurement. Proceed as directed under standardization of the ferrocyanide (*7*).

NOTES: (1) Samples 100 times the zinc titer make each ml of titrant equal to 1 per cent zinc.

(2) The aluminum displaces metals below aluminum in the emf series, e.g., lead, copper, cadmium, and bismuth, the ferrocyanides of which are insoluble. Iron is reduced to the ferrous state.

(3) Close control of the *p*H value is necessary to secure precipitation of the zinc.

(4) The ammonium thiocyanate may be omitted if only a little iron is known to be present.

(5) Particles adhering to the flask need not be removed.

(6) The end of the precipitation tube may need to be immersed in the acid for removal of adhering sulfide.

(7) Platinum and calomel electrodes may be used to determine the end point potentiometrically,

CHAPTER 28

GRAVIMETRIC METHODS

In gravimetric methods[1] of analysis, the analyst weighs either the desired constituent itself, or, more often, some compound bearing a known chemical relationship to the desired constituent.

It has been emphasized already, especially in Chapter 16, that weighing a substance is a very simple and relatively rapid operation. The operations that require more time, and often skill, in so many applied gravimetric methods are the preliminary treatment and the separation(s) required to yield a measurable product. Because of the importance of separations in gravimetric methods, the laboratory exercises in this chapter are subdivided according to the kind of method of separation employed. Representative examples are given of the four important types of separation discussed in Chapters 7-10.

VOLATILIZATION-GRAVIMETRIC METHODS

It was explained in the discussion of methods of making separations by volatilization[2] that a number of variations in the general procedure are made to fit the individual variations in the properties of the constituents being handled. The exercises that follow serve to exemplify some of these points.

Exercise 28.1. Determination of Water in Barium Chloride Dihydrate

The hydrate of barium chloride is homogeneous and stable at room temperature. Although the formula is usually written $BaCl_2 \cdot 2\,H_2O$, some analysts prefer the formula $BaCl_2(H_2O)_2$.

The water of crystallization may be volatilized at a relatively low temperature. With properly regulated heating, it is the only volatile

[1] See Chapters 3 and 16 for general discussions of weighing and gravimetry, respectively.
[2] See Chapter 7 for a general discussion of volatilization.

constituent. The determination consists, therefore, merely in finding the loss in weight on heating.

Many routine commercial determinations, e.g., determination of moisture in coal, are based upon this principle. Different temperatures are used, of course, to adapt the procedure to the properties of the constituents in the sample. Often the range is 105 to 110°.

The Sample

Selection and preparation. Select samples of well-crystallized commercial material.

Measurement. Place a porcelain crucible and lid (*1*) on the left-hand pan of the balance and weigh accurately (to four decimals). Transfer to the crucible about 1 g of the sample and reweigh the crucible. The difference is the weight of the sample.

The Desired Constituent

Separation. Place the crucible in a triangle (*2*) and heat by brushing a low flame across the bottom, the burner being held in the hand (*3*). Do not allow the crucible to reach redness nor heat with such rapidity that mechanical loss results from too sudden expulsion of the water. After heating for 15 to 20 min., place the crucible in a desiccator, put the lid on the crucible, cover the desiccator, and cool to room temperature (20 to 30 min.).

Measurement. Weigh the crucible and then repeat the heating and weighing until constant weight (*4*) is obtained. Calculate the percentage of water volatilized (*5*).

NOTES: (1) Before weighing, the crucibles should be heated to about the same temperature as that to be used later, and then cooled in a desiccator. They may be marked as directed on page 475 n.

(2) A crucible cover may be placed nearly over the top to prevent material from falling inside or gusts of wind from blowing out the finely powdered anhydrous residue. Also, possible loss from decrepitation is reduced.

(3) A more convenient and efficient method of heating is the use of an electric muffle furnace with automatic regulator set at 300°.

(4) For this quality of work, a variation of ±0.0002 g is satisfactory.

(5) If the theoretical percentage of water is 14.74, what might be indicated by an experimentally determined value of 15 per cent?

Exercise 28.2. Determination of Carbon Dioxide in Carbonates

The different methods that have been proposed for determining carbon dioxide in various materials include variations in the processes used, both to separate the gas and to measure its amount.

The preceding exercise illustrates one method of volatilization. Its application to limestone is described on page 566, including the advantages and disadvantages of the procedure. Since in many limestones more than mere evolution of carbon dioxide is likely to be involved, the process is referred to as "loss on ignition." It should be noted, of course, that the temperature required to evolve carbon dioxide from limestone is much higher than that specified for evolving the water of crystallization from barium chloride dihydrate.

In this exercise, the method described is capable of giving results of greater accuracy for carbon dioxide than is usually possible with heating alone. Two variations are given for handling the evolved gas. In both cases the evolution is accomplished by action of an acid on the sample, followed by heating.

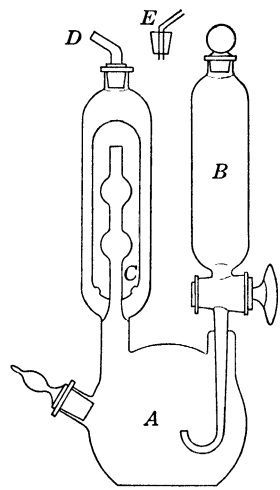


Figure 28.1

Alkalimeter. *A*, sample chamber; *B*, evolving acid; *C*, drying acid; *D*, outlet tube; *E*, inlet tube.

Method I

The first method is based upon the use of an alkalimeter, the Schroedter form of which is shown in Figure 28.1. Many other designs, more or less complicated, have been suggested. In the use of all devices of this type, the determination is made by loss, just as in the preceding exercise. With an alkalimeter, however, the aim is to have nothing leave the weighed system except the volatile desired constituent.

Briefly, the method involves putting the sample in chamber *A*, the evolving acid in bulb *B*, and sulfuric acid for drying outgoing gas in *C*. After weighing of the entire system, including the sample, the evolving acid is allowed to act upon the sample. The evolved carbon dioxide passes out through the concentrated sulfuric acid, being dried on the way. After dried air is passed through the solution of the sample to carry out all carbon dioxide, the system is reweighed.

Apparatus

Clean two alkalimeters, one for the sample and one for use as a counterpoise or tare. Nearly fill the drying bulbs with concentrated sulfuric

acid, and put in the other bulb somewhat more 20 per cent perchloric acid than will be necessary to evolve the carbon dioxide.

The Sample

Selection and preparation. Use the sample provided by the instructor.

Measurement. Weigh accurately an amount of sample such that the loss of carbon dioxide will be approximately 0.2 g. Transfer carefully to the evolution chamber of the alkalimeter.

Wipe the vessel lightly with a clean piece of slightly dampened, old muslin (*1*) and place in the balance for 20 min. (*2*). Counterpoise with weights and the blank alkalimeter (*3*) similarly prepared but containing no sample.

The Desired Constituent

Separation. After removing the alkalimeter from the balance, open the stopcock enough to permit the perchloric acid to drop slowly upon the sample. When all the material has reacted, warm the vessel somewhat. Replace the stopper in *B* with the inlet tube *E*. Then, by means of a rubber tube, connect the inlet *E* to a drying tower containing concentrated sulfuric acid (*4*). Connect an aspirator to outlet *D* and pull air through the apparatus for 30 min. at a rate not exceeding three bubbles per second.

Measurement. Again wipe the cooled alkalimeter and weigh it. From the loss in weight calculate the percentage of carbon dioxide (*5*).

NOTES: (1) An old bed sheet boiled in dilute hydrochloric acid and then alkali, and finally well rinsed in distilled water is very satisfactory for this purpose. New toweling is not very clean and leaves too much lint.

(2, 3) Difficulty is experienced in weighing glass vessels of this size. Wiping thoroughly enough to clean the surface may generate an electric charge. Time must be allowed for this charge to be dissipated and for the surface to reach equilibrium with atmospheric moisture.

(4) The air should be dried to the same extent before entry as it is when it leaves the flask.

(5) Although this method is reasonably rapid, its accuracy may not be entirely satisfactory. The large weight of the apparatus (approximately 75 g) decreases the sensitivity of the balance, the extensive area of the glass surface is difficult to clean reproducibly, and the outgoing gas may not be thoroughly purified and dried.

Method II

The methods of determining carbon dioxide that are generally considered most accurate for ordinary situations are based upon evolution

of the gas, removal of interfering gases, and measurement by some means. The gravimetric method described here consists in catching the evolved gas in a suitable absorbent, the increase in weight of which is then determined.

The assembly of apparatus for this determination is frequently designated as a "CO_2-train." Many variations have been made in the kinds of pieces used and in their arrangement. For student use the scheme illustrated in Figure 28.2 has been found convenient. Although the assembly is shown arranged in line, a more compact and portable arrangement is secured by fastening all the parts except the aspirator around a ring stand (see instructor's model).

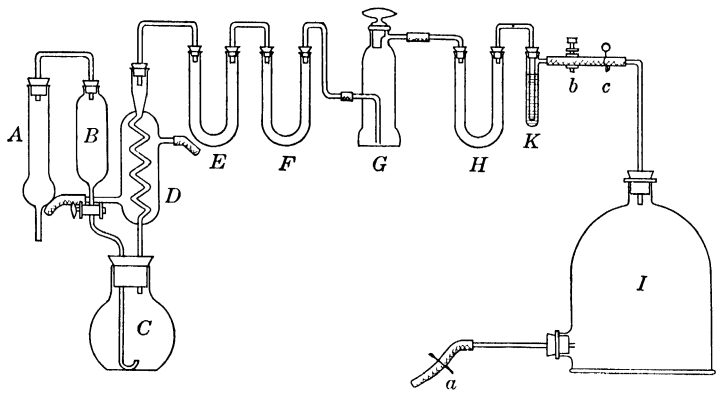


Figure 28.2

Apparatus for determining carbon dioxide by absorption. The drying tube *A* contains soda lime to remove carbon dioxide from incoming air. The dropping funnel *B* contains the acid for liberating the carbon dioxide. *C* is the evolution flask for the sample. *D* is a condenser for condensing most of the water vapor otherwise expelled from the flask. *E* and *F* contain calcium chloride (saturated with carbon dioxide) to dry the carbon dioxide. *G* is the absorption bulb, containing 4- to 8-mesh Ascarite (a patented absorbent consisting of sodium hydroxide and asbestos), soda lime, or caustic soda, with a layer of calcium chloride on the top. *H* is another drying tube that prevents moisture from coming back into the absorption bulb. The aspirator *I*, when filled with water, is used to pull the carbon dioxide through the system to the absorption bulb. *K* is a small bubble tube containing water, for judging the rate of passage of the gas. The clamps *a*, *b*, and *c* are for regulation of the flow of water and gas.

If hydrochloric acid is used to liberate the carbon dioxide, another tube must be placed between *D* and *E* (in Figure 28.2). It should contain an absorbent, such as concentrated sulfuric acid saturated with silver sulfate, for the acid vapor carried over. Some analysts prefer a 33 per

cent solution of potassium hydroxide for absorbing the carbon dioxide. This requires a different type of absorption bulb, which carries an additional calcium chloride tube to prevent moisture from leaving the bulb.

Another excellent example of this kind of method is the determination of carbon in steel. The sample is heated at 1000 to 1200° in a tube through which passes a stream of oxygen.

Apparatus

Before the sample may be secured from the instructor, the apparatus illustrated above should be assembled and approved. It must be airtight and neatly arranged (*1*). The aspirator bottle should be nearly full of water.

The Sample

Selection and preparation. See the preceding exercise.

Measurement. Weigh accurately about 1 g of the sample and brush it into the evolution flask. Add about 10 ml of water and replace the flask.

Treatment. Remove the absorption bulb from the train and close the inlet and outlet to the bulb to prevent entry of carbon dioxide (*2*). Wipe the bulb and place it in the balance 15 min. before weighing. In place of the absorption bulb insert a piece of glass tubing connecting *F* and *H*. With the screw clamp *b* set to allow two to three bubbles per second through *K*, open the clamp *a* and pull 500 ml of air through (*3*), as measured by the amount of water leaving the aspirator. During this interval weigh the absorption bulb (*4*).

The Desired Constituent

Separation. Replace the weighed absorption bulb in the train. Put about 50 ml of 10 per cent acid in the dropping funnel *B*, using sulfuric acid for samples that are soluble in it, and perchloric acid for those that are not (*5*). Open the clamp on the aspirator exit tube and then allow acid to drop slowly upon the sample (*6*). When 1 to 2 ml of acid remain in the funnel, close the stopcock. As soon as the sample seems to be decomposed, heat the evolution flask slowly to boiling, and maintain this temperature for about 1 min. Remove the flame and at the *same* time open the stopcock to allow the remaining acid to run into the evolution flask. Allow 1500 ml of water to flow out of the aspirator to draw all of the carbon dioxide into the absorption bulb (*7, 8*). Close the spring clamp *c*, remove the absorption bulb, and place it in the balance.

Measurement. At the end of 15 min. weigh the bulb and from the increase in weight calculate percentage of carbon dioxide (*9*).

NOTES: (1) The apparatus, as illustrated, consists of the following parts: straight drying tube, dropping funnel, evolution flask, condenser, three U-tubes, absorption bulb, bubble tube, aspirator, screw clamp, and two spring clamps.

(2) The outlet and inlet may be closed by means of short pieces of rubber tubing plugged with glass rod, or by a short policeman rubber, or the glass stopcocks that some bulbs have.

(3) Narrow strips of gummed label may be pasted on the aspirator at each 500-ml mark.

(4) To determine whether the absorption bulb can be handled reproducibly, a blank may be run by inserting the weighed bulb in the train, pulling 500 ml of air through it, and reweighing.

Use of a tare absorption bulb may facilitate the obtaining of reproducible weighings. Except for absorbing carbon dioxide, it is subjected to the same handling as the other bulb. It is placed on the right-hand pan of the balance, with whatever weights are necessary to counterpoise the other bulb.

(5) The solubility of the sample should be determined by a preliminary test.

(6) The rate of evolution may be judged by the bubble tube *K*.

(7) If Ascarite is used as the absorbent, the extent to which it has become exhausted is indicated by a change in its appearance.

(8) If 33 per cent potassium hydroxide solution is the absorbent, its maximum safe capacity for absorption may be assumed to be 0.1 g of carbon dioxide for each milliliter of solution in the bulb.

(9) Some analysts prefer to check the operation of such equipment with a sample of known analysis. In this case, the standard sodium carbonate or calcium carbonate recommended for the standardization, respectively, of hydrochloric acid or potassium permanganate may be used.

PRECIPITATION-GRAVIMETRIC METHODS

The general principle of all precipitation-gravimetric[3] methods is the separation by precipitation of the desired constituent, usually in the form of an insoluble compound and, rarely, as the constituent itself. The precipitate is then dried or ignited to constant weight, when the desired constituent usually is weighed as such, or in the form of a compound bearing a known relationship to the desired constituent. In rare instances the residue weighed is an element other than the constituent desired, but the latter can be calculated from the weight obtained.

General Technic[4]

Precipitations are usually made in beakers by adding a solution of the precipitant dropwise from a pipet to a hot solution that is being stirred.

[3] See Chapter 8 for a general discussion of precipitation.

[4] Before the first precipitation-gravimetric procedure is undertaken by a class, demonstration of various manipulative details is desirable. Preferably, this should be done for the individual student at the time he is ready to handle his first precipitate. With large classes, however, this may not be feasible.

Small groups may be shown the main features of the process by means of a lecture

Some precipitants are handled more conveniently by a medicine dropper. Certain precipitates separate on changing of the nature of the solvent. Babbitt metal dissolves in concentrated sulfuric acid; however, on dilution with water, the lead sulfate precipitates. Its solubility is further reduced by adding an equal volume of 95 per cent ethanol.

Digestion. Nearly all precipitates require more or less digestion to complete the precipitation and make all the particles of filterable size. The process may be carried out by setting the beaker aside for 10 to 24 hrs. at room temperature, unless long standing is likely to result in entrainment through postprecipitation of some constituent, or in dissolution of some contaminant from the beaker. If a higher temperature changes the composition of the solvent, standing at room temperature may be necessary. Stirring accelerates the action. This effect is especially striking with silver chloride.

Whenever higher temperatures are permissible, digestion is usually done near the boiling point of the solution. The vessel may be placed over a low flame, unless bumping interferes. Open steam baths are widely used. Hot plates, heated by gas, electricity, or high-pressure steam, are common laboratory appliances used for digestion. Beakers containing precipitates should be covered with a watch glass during digestion, with the convex side turned down. Clearing of the supernatant liquid usually indicates adequate digestion, if a drop of precipitant produces no further precipitation. Filterability is the ultimate test.

Unless experience has shown the precaution to be unnecessary, a filtrate should not be discarded until it has stood long enough to allow any finely divided precipitate to settle out. Photochemically sensitive precipitates should be protected from irradiation with strong light.

Filtration. Following digestion, the next operation is filtration. For this purpose, paper is the most common filtering medium. Although good-quality paper is spoken of as being ashless, it always leaves a nonvolatile residue. The advertised ash, in grams, for several kinds of 9-cm paper follows: J. Green, 0.00014; Schleicher and Schüll, 0.00011; Whatman, 0.000057; "Delta," 0.000053; and Munktell, 0.000030.

The physical state of precipitates varies so much that paper of different densities is made to provide for the different conditions encountered. Figure 28.3 is a rough schematic representation of different physical states of precipitates. Included are general recommendations for the number

demonstration. For larger numbers the author uses a motion picture, the specific example being the precipitation and handling of silver chloride (the first precipitation-gravimetric determination to be done in the laboratory). The items covered include both the preparation of the Gooch crucible and the main operations on the precipitate, such as precipitation, digestion, filtration, transfer, washing, and drying the silver chloride.

of Schleicher and Schüll quantitative-grade papers to use for the different kinds of precipitates.

The recommendations for four grades of Whatman quantitative paper follow: No. 40 for general work; No. 41 for gelatinous, large-particle precipitates; No. 42 for fine precipitates; and No. 44 for the most precise determinations in general work, or for fine precipitates. Other makes of paper come in similar grades.

Long, narrow-stem funnels work well. Washington recommends[5] particularly funnels with a circle in the stem, for holding the column of liquid. Grooved funnels increase the rate of filtration. The tip of the stem should touch the beaker wall to prevent splashing of the filtrate.

Paper is usually folded as illustrated in Figure 28.4, with one edge torn back to produce a better fit in the funnel. If the funnel angle is just 60°, as most funnels are now made, the paper may be folded as shown at the left in Figure 28.4. Otherwise, the edges cannot come together, as shown at the right in Figure 28.4. It is important that the paper fit well enough to hold a column of water the length of the stem in order that the filtration may be made as rapidly as possible.

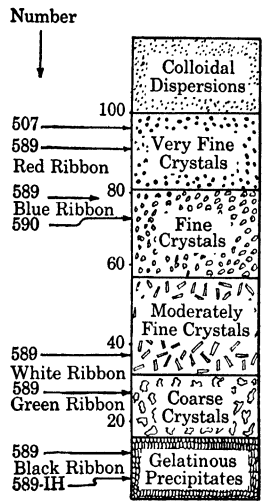


Figure 28.3

Relative values of retention of S and S ash-free quantitative analytical filter papers.

Some analysts prefer to fold the paper according to the quadruplet method. Figure 28.5 illustrates three stages in the process. More rapid filtration is claimed for such a paper.

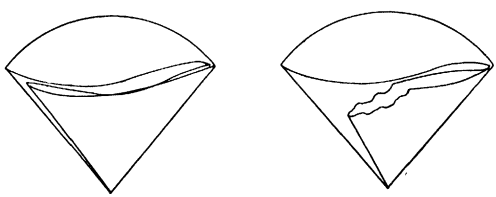


Figure 28.4

Usual method of folding paper.

Many precipitates, well digested, filter rapidly on the proper grade of paper. Crystalline precipitates are likely to work best.

Gelatinous precipitates may cause much trouble by clogging the pores

[5] Washington, *The Chemical Analysis of Rocks*, p. 41, Wiley, 1930.

of the paper, thus greatly reducing the rate of filtration. Some authors recommend adding ashless paper pulp to such a precipitate before filtration. An extra paper may be torn up and then disintegrated in the solution. "Filter aids," made of paper, are available to use in a solution for this purpose.

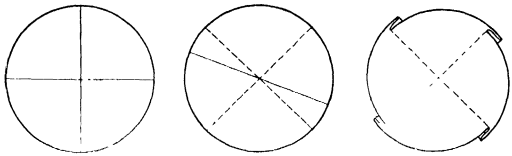


Figure 28.5

Quadruplet method of folding paper.

Filtration under reduced pressure is not as common with paper filters as with inorganic media. Figure 28.6 shows a bell jar on a glass plate arranged to receive the filtrate in a beaker. A filter flask, shown in Figure 28.7, with a funnel and rubber ring for holding the crucible, may be used. As wet paper has low tensile strength, the tip must be supported. A platinum or tantalum cone, placed in the bottom of the funnel, is most convenient. A small, hardened paper, or a piece of muslin, may be folded with the paper to give a supporting cone when the paper is put in the funnel.

Inorganic filtering media are widely used. The Munroe all-platinum

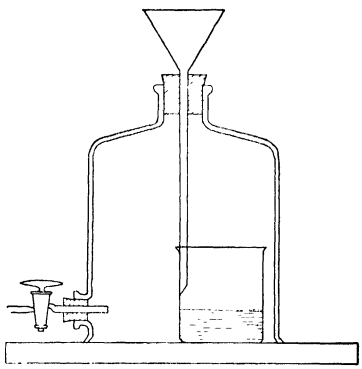


Figure 28.6 (above)

Bell jar for suction filtration.

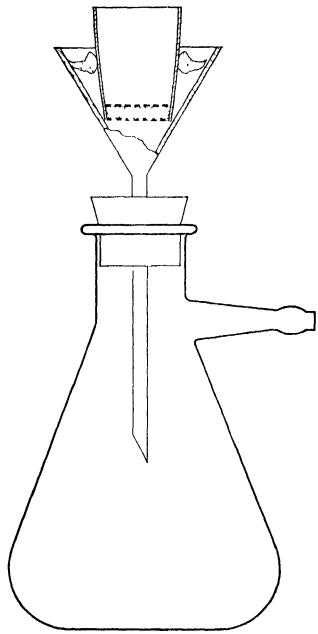


Figure 28.7 (right)

Filter flask with Gooch crucible.

crucible[6] is undoubtedly the best but it is used ordinarily only for the most exacting work. The most common medium of this type consists of a mat of acid-washed, long-fiber asbestos on the perforated bottom of a porcelain crucible. This device is usually called a Gooch crucible, after the well-known analyst, F. A. Gooch. It is generally recommended, except where the solution is sufficiently alkaline to have some solvent action on the asbestos, or where a precipitate, such as hydrous aluminum oxide, must be ignited to a very high temperature (about 1200°) to insure complete dehydration.

Figure 28.8 shows a section of a Gooch crucible. To prepare the mat, the crucible is placed in some device (e.g., that shown in Figure 28.7) by means of which air may be drawn through the holes. A portion of asbestos, suspended in water, is poured into the crucible, after which the analyst turns on the water pump, or uses some other means of obtaining suction, and sucks out the water. It is necessary to guess at the amount to use. The amount should be sufficient to hold the precipitate, but not enough to slow up the rate of filtration unduly. For good-quality fiber, it is generally satisfactory to use an amount such that, when the crucible is held with the bottom toward the light, the location of the holes can just be distinguished. When this point is reached, it is desirable to press a perforated porcelain plate down on the mat to prevent the mat from being stirred up during washing. The crucible is then washed and dried or ignited under the *same* conditions that are to be used for the precipitate. According to some writers, long ignition at high temperatures makes asbestos slightly soluble.

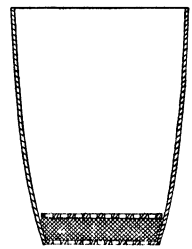


Figure 28.8

Section of a Gooch crucible.

Filter pads of glass fibers are now available as a substitute for the asbestos mat in the Gooch type of crucible. They have not yet had extensive use.

Several other kinds of inorganic media are available. Alundum crucibles are used occasionally; however, since they are entirely unglazed, they are difficult to wash thoroughly. Crucibles made of heat-resistant glass, with a sintered glass bottom, are useful if the temperature does not have to go much above 500°. The best of this type of crucible is of porcelain with glazed sides. Several porosities provide for different sizes of particles of precipitate. Most recent of this kind of crucible is one made of

[6] Hillebrand, Lundell, Bright, and Hoffman, *Applied Inorganic Analysis*, p. 101, Wiley, 1953.

stainless steel. All of these crucibles have important uses, but precipitates, such as barium sulfate, are difficult to remove.

Washing. Most precipitates are produced in the presence of one or more soluble compounds. Since the latter are frequently not volatile, at least at drying temperatures, the precipitate is always washed to remove such material as completely as possible.

Water is the washing medium often used. Dilute solutions of electrolytes, such as volatile acids, ammonium hydroxide, and ammonium salts, may be necessary to prevent dispersion of the precipitate or to reduce solubility through the common-ion effect. Ethanol may serve to keep the solubility low. When the precipitate is to be air-dried rapidly, the washing may be completed with ethanol, followed by diethyl ether. Magnesium ammonium phosphate hexahydrate is handled in this way.

In general, the washing medium should meet the following requirements, insofar as possible: (1) have no solvent action on the precipitate; (2) be easily volatile at the temperature of drying or igniting of the precipitate; (3) dissolve the undesirable substances easily; (4) have no dispersive action on the precipitate; (5) form no volatile or insoluble product with the precipitate; and (6) contain no substance to interfere with subsequent determinations in the filtrate.

The method used in washing a precipitate is of some importance. If the material settles fairly rapidly and tends to clog the filter, washing by decantation is recommended to remove most of the soluble matter. The procedure consists in pouring the liquid through the filter without transferring the precipitate. Another portion of washing liquid is added, the precipitate is stirred well, and is then allowed to settle. After pouring off of the clear liquid, the process is repeated as many times as necessary. Crystalline precipitates are generally transferred to the filter at once, without washing by decantation. Finally the precipitate is washed out of the beaker to the filter by means of a small stream of washing liquid directed from a wash bottle.

To continue the washing, the wash-bottle stream is directed to stir up the precipitate in order to secure thorough contact of the liquid with all particles.

Some precipitates cause difficulty by adhering to the surface of the beaker. Generally they may be removed by rubbing with a "policeman," which consists of a piece of rubber tubing closed at one end, fitted on a stirring rod. When the precipitate is filtered on paper, it is advantageous occasionally to wipe out especially adherent particles with a small piece of ashless paper, which is then added to the bulk of the precipitate.

The question of how much washing liquid to use always arises. The

amount must be sufficient to remove the constituents to be eliminated. It should be kept at a minimum, however, because of the time consumed by washing and because any washing necessarily dissolves slight amounts of the precipitate. If a given amount of washing liquid is to be used, it is better added in a number of small portions rather than all together.[7] The precipitate should drain somewhat between each portion. Gelatinous precipitates must be watched when this practice is followed. If they are sucked too nearly dry, cracking or channeling will occur, thus allowing the liquid to run through without washing the mass of the precipitate.

Complete washing is accomplished much more readily with some precipitates than with others. Until the analyst has learned by experience what is necessary, completion of the process must be tested. Ordinarily this test is made by removing a few drops of the most recent filtrate and applying some qualitative reagent. If a beaker is the receiving vessel for the filtrate, a test tube is substituted to obtain the test portion. If a suction flask is used, the test tube may be suspended inside the flask by means of a thread or fine wire. Obviously, the analyst should test for some constituent being washed out. Preferably, the one selected will be present in relatively large amount and be susceptible to easy testing.

Drying and ignition. The final operation in precipitation separations, if the desired constituent is to be measured gravimetrically, consists in bringing the residue to a weighable condition. This result is accomplished by *drying* or *igniting* the precipitate. The term used for the process depends on the temperature at which the precipitate is heated. There is no definite point below or above which the material may be said to be dried or ignited. Generally, however, analytical procedures will be found to designate *drying* if the temperature is below 250°. Ignition applies to temperatures from 250° to the maximum attainable.

Drying is confined almost exclusively to precipitates that can be handled as such, and require only enough heating to eliminate any washing medium adhering to the particles. Representative examples of such precipitates are silver chloride and lead chromate. These compounds, along with many others, are dried at 105 to 110°. Air-drying at room temperature is an exceptional practice, but it is recommended for magnesium ammonium phosphate hexahydrate when it has been washed with ethanol and diethyl ether. Precipitates to be dried to constant weight are always filtered on an inorganic medium.

Electrically heated and regulated ovens are now used almost exclusively for drying (see Figure 7.1, page 78). Precipitates are ignited at temperatures above 250° for several reasons. All substances filtered on

[7] Waldbauer and Cortelyou, *J. Chem. Educ.*, 18, 341 (1941).

paper must be handled in this way. There may be no transformation in the precipitate itself, but the high temperature is required to volatilize traces of solvent and/or to burn out the paper. Barium sulfate is an example of a precipitate to be treated by ignition. Many precipitates cannot be dried and weighed as such, because of their uncertain composition. Such compounds are ignited at a temperature high enough to transform them to a substance of definite and known composition. The magnesium ammonium phosphate hexahydrate, when heated in a Gooch crucible at 900°, is converted to the pyrophosphate, $Mg_2P_2O_7$. At the same temperature calcium oxalate, $CaC_2O_4 \cdot H_2O$, is decomposed to the oxide. Certain substances, such as hydrous aluminum oxide, lose their water completely only at considerably higher temperatures. Ignition, at least in the lower range of temperatures, may be necessary also to eliminate the electrolyte used in the washing medium for certain precipitates.

The devices used for attaining ignition temperatures include various kinds of gas burners and electric furnaces. Burners of the Tirrill, Meker, and blast-lamp types are illustrated in Chapter 7 (pages 79-80). These devices suffice for nearly any ordinary ignition. Electric muffle furnaces are very convenient where a number of precipitates are to be ignited at the same temperature. Such equipment, also illustrated in Chapter 7 (page 78), will operate day after day at 900 to 1000° without burning out the heating element. Some precipitates, such as lead sulfate, will not withstand the temperature even of a Tirrill burner, nor do they decompose completely. In such cases, an electric furnace regulated for a permissible temperature must be used, or some kind of air bath heated with a burner must be arranged. Lead sulfate in a Gooch crucible may be heated at about 600° by suspending the crucible in an asbestos ring placed inside a larger crucible. The larger crucible is then heated with a Meker-type burner.

Crucibles. When an inorganic filtering medium is used, the precipitate is transferred directly to the device in which the drying or ignition is to be done. Substances filtered on paper must be transferred, along with the paper, to a crucible in which to burn the paper and bring the material to constant weight. Several kinds of materials are used for making crucibles.

The most common crucibles are made of porcelain. They are cheapest and give good service when handled properly. Some reactions, such as alkaline fusions and volatilizations with hydrofluoric acid, cannot be made in porcelain because of the resultant chemical attack. Cold crucibles brought too quickly into a hot flame may crack. New crucibles that

are to be used at a high temperature must first be brought to constant weight at this temperature, as there is generally an appreciable decrease in weight from loss of volatile material. A stock of new crucibles usually must be given some distinguishing mark.[8]

Crucibles made of fused silica are more expensive than porcelain. They are especially advantageous in that they have a high resistance to heat shock. Silica ware is somewhat less soluble than porcelain and is sometimes used for evaporation as a substitute for platinum, when the latter is unavailable.

In some respects, platinum is the most valuable metal for apparatus for analytical work. A platinum alloy containing several per cent of rhodium is somewhat harder than platinum alone and is also more resistant toward reagents. In the form of crucibles, dishes, and electrodes, and other apparatus, platinum is widely used; its cost is the chief factor preventing even more extensive use. Platinum crucibles are practically a necessity for such operations as alkaline carbonate fusions and volatilizations with hydrofluoric acid. High thermal conductivity is an incidental advantage. As platinum is slighly volatile at high temperatures, a small loss may be detected in crucibles ignited for long periods at 1000°. There is a slight loss whenever fusions are made with compounds such as sodium carbonate or potassium pyrosulfate. In the latter case, enough platinum may be removed to give the acidified solution of the fused mass a yellow hue. A few reagents, such as *mixed* hydrochloric and nitric acids or others liberating chlorine, attack platinum seriously.

The directions for care and use of platinum ware in the accompanying note were provided by the Baker Platinum Works.[9]

NOTE ON THE CARE AND USE OF PLATINUM: Platinum is not oxidized in the air at any temperature nor attacked by any single acid.

The caustic alkalies, the alkaline earths, nitrates, and cyanides, and especially the hydroxides of barium and lithium attack platinum at red heat, although the alkaline carbonates have no effect at the highest temperatures.

Phosphorous and arsenic attack platinum when heated with it. Therefore, phosphates, arsenates, and similar compounds should not be ignited in their filter paper in a crucible.

[8] NOTE ON MARKING PORCELAIN: Although file marks on the edge may be used, porcelain crucibles are marked most satisfactorily by burning some colored compound into the glaze. Ink containing iron, or a solution of an iron salt, may be placed in *very* small dots on the crucible and then warmed to evaporate the solvent. Subsequent ignition in a hot flame will burn the dots into the glaze in the form of brown ferric oxide. Instead of the iron solution, another solution may be made by adding 2 ml of water glass to 10 ml of water, stirring, acidifying to litmus with nitric acid (1:1), and adding 15 ml of saturated potassium dichromate.

[9] See also, Lange, *Handbook of Chemistry*, p. 1814, Handbook Publishers, 1952; and Notes on the Care and Use of Platinum, J. Bishop and Co.

Silicon, which may be formed by the reducing action of carbon on silica, causes brittleness.

Contact with compounds of easily reducible metals like lead is dangerous at high temperatures, as low-fusing alloys are readily formed with the platinum.

Platinum should not be put in the inner cone of a Bunsen flame, as the carbon reacts with the platinum to form a carbide which causes brittleness and general deterioration.

Cleaning. Platinum ware should be cleaned and polished immediately after using. Long heating in the Bunsen flame gives the surface of platinum the familiar gray appearance which cannot be removed except by burnishing. Rubbing the surface with moist *round-grain* sea sand, applied with the finger, serves to remove most impurities and to polish the metal without material loss in weight.

Iron stains or similar basic material may be removed by fusing with potassium pyrosulfate (or potassium hydrogen sulfate heated long enough to expel the water), dissolving the cooled mass in boiling water, and polishing with sand. The outer surface must be placed in the pyrosulfate fused in a dish.

Materials essentially acidic in nature, such as adhering silica, may be fused with sodium carbonate or borax and then dissolved in hydrochloric acid.

The cleaning action of sodium amalgam may be utilized by rubbing the amalgam upon the metal with a cloth, and then moistening with water, which attacks the sodium and leaves the mercury to alloy with foreign metals. The mercury is then wiped off and the article cleaned and polished with sand.

If the existence of a base metal alloyed with platinum is suspected, immerse the article first in boiling hydrochloric acid for a few minutes; then, after thoroughly rinsing with water, immerse in boiling nitric acid. If the artcle is unaffected in weight or appearance, and the acid baths fail to give reactions for the base metals, the absence of such is assured.

In a number of special cases other materials have been used for crucibles. The applications are so limited, however, that such vessels are not included in this book.

Burning paper. Burning a filter paper would seem to be a very simple matter. Actually it often is not. The paper itself may not burn well in contact with a precipitate, and the oxidation of the organic matter may exert some chemical action on the precipitate. Thus, stannic oxide is very easily reduced, and magnesium pyrophosphate has long been noted for yielding a dark residue unless it is ignited carefully with paper.

If the soluble salts have been well washed out of the paper, burning it successfully is largely a matter of control of temperature and rate of ignition. Conditions vary somewhat for different precipitates, but in any case the first operation is to fold the paper and press it down in the crucible without losing any precipitate.

Washington[10] recommends placing the crucible in an upright position

[10] Washington, *Chemical Analysis of Rocks*, p. 118, Wiley, 1930.

on a triangle[11] on a ring the height of which above the burner can be adjusted. With the cover slightly aside, the crucible is then heated with a low flame in order to dry out the washing liquid. The ring is lowered gradually as the charring of the paper proceeds. When charring is complete, the crucible and contents are heated gradually to higher and higher temperatures. Completion of the ignition process is marked by disappearance of all black particles of the paper and by attainment of constant weight by the residue. Failure to do the initial heating slowly may produce a dark residue that is practically impossible to burn out.

Many analysts prefer to place the crucible and the lid on the triangle in an inclined position, as shown in Figure 28.9. To dry out and burn the paper, a low-flame burner is placed in position *A*. The hot air deflected into the crucible by the lid leaves through the opening at the top. When charring is well advanced, the burner is moved to position *B*. The flame is turned up gradually as the paper burns out. When all black particles disappear, the crucible is placed in an upright position and covered with the lid. The full flame is used to achieve constant weight.

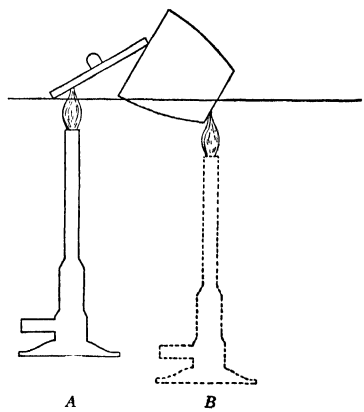


Figure 28.9

Position of crucible for burning paper.

Chemical changes during ignition. Ignition of precipitates along with filter paper may produce several chemical changes. There is always the burning of the paper, accompanied by elimination of the excess washing medium. Some precipitates are perfectly stable under these conditions, but many are not. The two general kinds of chemical change encountered are reduction and decomposition.

Barium sulfate is said to be stable, even beyond 1200°, in a good oxidizing atmosphere. If it is heated in the presence of paper in a crucible enveloped in a large flame from a Meker burner, partial reduction occurs. Stannic oxide is easily reduced to metallic tin in the absence of sufficient oxygen. When residues are known to be easily reduced, some analysts recommend moistening the paper, before ignition, with a

[11] Triangles are usually made of fused silica rods or tubes on a wire, of nickel-chromium wire, or of clay tubes on a wire. For student use the alloy is the most serviceable, but crucibles heated on it should be watched to see whether any particles from the wire stick to them. The triangle must be clean and free of iron.

few drops of concentrated nitric acid or a saturated solution of ammonium nitrate. Heating alone in air will reoxidize some reduced residues. The addition of a few drops of concentrated nitric acid, repeated if necessary, will help in such cases as partially reduced ferric oxide. The oxidation of any remaining carbon is likewise aided. Incomplete oxidation of carbon, resulting from fusion of unremoved precipitant around the particles, has been given as the explanation for "black" magnesium pyrophosphate. In some cases, at least, dark residues of silica have been attributed to the formation of silicon carbide.

Decomposition reactions are either prevented or brought to some definite stage through control of the ignition temperature. Calcium oxalate is converted at 900° to the oxide. At 525° to 550° the transformation stops quantitatively with the formation of calcium carbonate. Excessive temperatures during ignition may volatilize the residue, as with silver chloride, or may produce incomplete and indefinite decomposition, as with lead sulfate.

Cooling residues. Dried or ignited residues are always cooled to *room* temperature before weighing. Cooling is accomplished by placing the crucible in a desiccator (see Chapter 21, Figure 21.3) for 20 to 30 min.

Exercise 28.3. Determination of Chloride Ion

In the method under consideration, the chloride ion is precipitated by means of silver ion as silver chloride in a solution acidified with nitric acid, filtered on a Gooch crucible, dried to constant weight at 105°, and weighed as such.

Probably the properties of no other precipitate have been studied so thoroughly as those of silver chloride. The most commonly used chemical method for determining atomic weights consists in preparing a pure chloride of the element to be measured, precipitating the chloride from a known weight of the compound with silver nitrate, and weighing the silver chloride. By means of the standard values for silver and chlorine, the unknown value may be calculated.

The converse of this method is used for determining silver, employing hydrochloric acid as the precipitant. Too much precipitant may dissolve some precipitate as a complex $HAgCl_2$. Although the solubility of both silver bromide and silver iodide is less than that of the chloride, the latter is used for quantitative determinations of silver since it is the most stable photochemically. The common-ion effect indicates that a small excess of precipitant will counteract any deficiency of solubility.

If this general procedure is used for bromide or iodide, the precipitate

should be protected, insofar as possible, from light. The compounds are more sensitive to light than is silver chloride.

Apparatus

To prepare a Gooch crucible, connect a suction flask to the water pump (see page 471) and include a trap between the flask and pump (consult instructor). Insert the crucible in the device provided for use in the flask (*1*), apply *gentle* suction, and pour some of the asbestos suspension (*2*) into the crucible (*3*). When enough has been added, place a perforated disc in the crucible and press it down on the asbestos (*3a*). Wash the crucible thoroughly with 0.01 *M* nitric acid. Turn off the suction, remove the crucible, wipe off the outside, and bring the crucible to constant weight at 105° in an electric oven.

The Sample

Selection. Select a suitable representative sample of the material to be analyzed.

Measurement. From a bottle of sample, dried at 105°, weigh accurately on a watch glass a sample of such size that a residue of silver chloride of at least 0.1 g will be obtained (*4*). Transfer to a clean (*5*) 250-ml beaker.

Treatment. Add about 75 ml of water to dissolve the sample. Then add two drops of ordinary methyl orange indicator (*6*) and just enough dilute nitric acid (*7*) to make the solution acidic.

The Desired Constituent

Separation. To the unheated solution (*8*) add from a pipet, dropwise and with stirring, enough 5 per cent solution of silver nitrate to complete the precipitation (*9*). Place the beaker on the steam hot plate (*10*) to digest until coagulation leaves a clear solution. Test for *completion* of precipitation by adding another drop of precipitant.

Place the weighed Gooch crucible on a holder of a *clean* (*11*) suction flask and apply gentle suction. Pour most of the supernatant liquid into the crucible and then wash out all of the silver chloride with 0.01 *M* nitric acid (*12*). Use a policeman to loosen adhering particles. Wash the precipitate until a portion of the washings (*13*) shows no more than a faint turbidity when tested with hydrochloric acid. Dry the crucible and precipitate in an oven at 105°.

Measurement. Weigh the precipitate of silver chloride and reheat to constant weight (±0.0002 g). Calculate the percentage of chloride.

NOTES: (1) A rubber ring made for use in an ordinary funnel is convenient for Gooch crucibles.

(2) Only the best grade of acid-washed asbestos, specially prepared for this kind of work, should be used.

(3) The amount of asbestos needed depends upon its physical state and the fineness of the precipitate to be filtered upon it. Generally the mat should be at least 1 to 2 mm thick to hold fine precipitates. On holding the end of the crucible toward a light, one should not be able to see more than the bare outline of the holes in the bottom. Mats too thick require too much time for filtration.

(3a) If available, a glass fiber disc may be used instead of the asbestos.

(4) Ordinarily samples of 0.3 to 0.4 are satisfactory. A quick check on an unweighed portion of sample will show whether the amount of chloride present is large or small.

(5) Beakers may be cleaned conveniently by rubbing the inside surface with a little sodium hydrogen carbonate paste or finely ground pumice stone and then rinsing *thoroughly*. Dichromate cleaning solution may be used, if necessary.

(6) For this kind of work, modified methyl orange may not be satisfactory. In case the indicator compound is destroyed by some chemical action, the dye alone may be left. The solution remains colored, but without indicating the degree of acidity.

(7) Both the distilled water and the nitric acid should be tested for the presence of chloride ions.

(8) Boiling might cause loss of hydrochloric acid.

(9) The completion of precipitation is not directly visible, but small excess of precipitant produces a rather characteristic coagulation The precipitate should be protected from direct sunlight. Photochemical action darkens the precipitate, with the formation of some $AgCl \cdot Ag$.[12]

(10) Digestion over a low flame is satisfactory. Occasional stirring aids coagulation.

(11) It may be necessary to re-filter the solution if fine particles go through at first.

(12) Washing with cold water alone peptizes the precipitate, thus causing the particles to run through the filter.

(13) A cloudy filtrate indicates a thin mat or inadequate coagulation. Digest the solution further by gentle boiling and re-filter it.

Exercise 28.4. Determination of Sulfate Ion

The sulfate radical is most frequently determined by precipitation as barium sulfate and weighing it as such. The precipitation is made by means of barium chloride from a solution slightly acidified with hydrochloric acid to prevent the formation of such compounds as barium carbonate. The method is often used for determining sulfur in various

[12] See Lundell and Hoffman, *Bur. Standards J. Research* **4**, 109 (1930), for an account of the extent of such action.

materials in which the element can first be oxidized to the form of sulfate.

Barium sulfate is particularly susceptible to contamination by adsorption of soluble salts in the course of the formation of the precipitate. Anions, especially nitrate, cause positive errors. The reverse effect is produced by cations. When much iron is present, the ignited residue may be quite brown. Chapter 8 contains a discussion of the errors arising from such entrainment. The precipitate tends to "creep" out of the filtering vessel and be lost.

During ignition, the precipitate is subject to reduction to the sulfide, especially if paper is used for filtration and the ignition is made without adequate air supply, as is the case when the crucible is covered too closely or is enveloped by the large flame of a Meker-type burner. Conversion of any partially reduced material may be accomplished by ignition with free access of air. Addition of two drops of concentrated sulfuric acid, followed by ignition, reconverts any reduced material.

Apparatus

Prepare the mat in a Gooch crucible as directed in the previous exercise. Ignite to constant weight by placing the crucible in an inverted crucible cover and heating the latter to redness over a Tirrill-type burner.

The Sample

Selection. Use the sample provided by the instructor.[13]

Measurement. Weigh accurately about 0.3 g of the dried material and transfer to a 250-ml beaker.

Treatment. Dissolve in about 75 ml of water. Add a drop of methyl orange indicator and enough hydrochloric acid to make the solution slightly acidic (*1*).

The Desired Constituent

Separation. Heat the solution to incipient boiling (*2*) and add, dropwise and with continuous stirring, enough 5 per cent barium chloride solution to complete the precipitation. After precipitation, add dropwise, 1 ml of a solution of agar-agar (*3*); stir the suspension for 10 sec., after each drop, to facilitate coagulation. Digest the system until the supernatant liquid is clear. Filter the precipitate (*4*) on the weighed crucible (*5*), wash with hot water until free of barium (*6*), and ignite under the same conditions used in preparing the crucible.

[13] The heading "Selection" is used throughout the book in order to keep before the student the fact that selection of a sample is always the first operation in applied analysis. Actually, in elementary courses prepared samples are usually dispensed by the instructor.

Measurement. Weigh the crucible and repeat the heating to constant weight. Calculate the percentage of sulfate.

NOTES: (1) The solution must remain acidic during precipitation and digestion. Too much acid increases the solubility of the precipitate, presumably as a result of the formation of some hydrogen sulfate. Solubility in concentrated sulfuric acid is attributed to the formation of a complex, $H_2Ba(SO_4)_2$.

(2) The addition of 5 ml of a saturated solution of picric acid at this point seems to aid in producing particles of larger size. The precipitant may be added rapidly and the precipitate can be filtered after boiling the solution gently for 10 min.

(3) A satisfactory concentration is 1 g per liter.

(4) Creeping of the precipitate is likely to be troublesome with barium sulfate.

(5) Many analysts prefer to filter the precipitate on paper. A high-grade paper must be used for such finely divided precipitates. Whatman No 42, or Schleicher and Schüll No. 589, Blue Ribbon, is recommended.

(6) What is a satisfactory test for the barium ion here?

Exercise 28.5. Determination of Calcium

In contrast to the preceding two methods for determining chloride and sulfate, the gravimetric procedure for calcium, which involves precipitation of the element as the oxalate, $CaC_2O_4 \cdot H_2O$, illustrates three important variations in the over-all operations. In the first place, although ammonium oxalate is actually used for the precipitation, the precipitant may be considered as an organic compound,[14] for one might use oxalic acid, $H_2C_2O_4$, and then adjust the *p*H to about 6. In the second place, hydrolysis of urea is used to raise the *p*H slowly in order to obtain the precipitate in good condition for filtering. The process illustrates homogeneous precipitation from solution. In the third place, although it is possible to weigh the precipitated monohydrate as such, practically all standard works specify conversion to another form that can be handled more readily.

Several possibilities are available for the chemical transformation of the monohydrate. Apparently, volatilization of the water alone, to leave the anhydrous oxalate, is not readily feasible. Ignited at 525°, the precipitate decomposes according to the equation

$$CaC_2O_4 \cdot H_2O \rightarrow CaCO_3 + CO\uparrow + H_2O\uparrow$$

The carbonate thus formed is relatively stable under ordinary weighing conditions and is weighed as such. The method much better known consists in heating the precipitate at 900 to 1000°, where the decomposition proceeds according to the equation[15]

[14] See Exercise 28.7 for use of dimethylglyoxime, another organic precipitant, for determining nickel.

[15] See texts in physical chemistry for a discussion of the equilibrium conditions of this important system.

$$CaC_2O_4 \cdot H_2O \rightarrow CaO + CO_2\uparrow + CO\uparrow + H_2O\uparrow$$

The oxide has the merit of stability at any temperature likely to be reached above 1000°; however, it must be weighed rapidly, even in a covered crucible, because of its ready absorption of carbon dioxide and water to form the carbonate and hydroxide, respectively. Some analysts recommend conversion of the precipitate to the sulfate, $CaSO_4$, by heating in the presence of an excess of sulfuric acid at a temperature just high enough (350°) to volatilize the excess acid.

Because of the solubility of calcium oxalate, the precipitate is washed with a dilute solution of the precipitant, in order to take advantage of the common-ion effect.

Apparatus

If the oxide is to be weighed in porcelain crucibles, the marked crucibles and lids should be heated to constant weight in a Meker-type burner or in an electric furnace at about 900°. If the carbonate is to be weighed, use clean porous-bottom porcelain crucibles of fine porosity, heated at 525° to constant weight.

The Sample

Selection. Use the sample provided by the instructor.

Measurement. Weigh accurately on a watch glass samples of about 0.5 g and transfer them to marked 400-ml beakers.

Treatment. Add about 75 ml of water, cover with a watch glass, and add 10 ml of 10 per cent hydrochloric acid. When the sample dissolves, boil the solution gently for 1 to 2 min. to expel any carbon dioxide (*1*), and dilute to about 150 ml with distilled water.

The Desired Constituent

Separation. Heat the solution nearly to boiling and add about 1 g of ammonium oxalate dissolved in about 50 ml of water (*2*). To the hot solution add *filtered* (*3*) 6 *M* ammonium hydroxide until the calcium oxalate *just begins* to precipitate. Now add 15 g of urea and digest on the steam hot plate for 1 hr. Add two drops of methyl red solution. If the solution turns pink, add filtered 6 *M* ammonium hydroxide, dropwise with stirring, until the solution just turns yellow. Test for complete precipitation by adding a few drops of the ammonium oxalate solution. Proceed by Method I or Method II, as follows.

Method I. Determination as the oxide. Filter the solution through filter paper (Whatman No. 42, or equivalent), transferring to the paper

as much of the precipitate as possible. Prepare a 0.1 per cent ammonium oxalate washing solution. Use it, at room temperature, to complete the transfer of the precipitate to the paper, and to wash the precipitate until 1 ml of the last washings shows no test for chlorides (*4*).

Transfer the precipitate and paper to a porcelain crucible (weighed with lid) placed upright in a triangle. Place the cover on the crucible so that only a very narrow opening remains, and heat *slowly* with a Tirrill burner until the contents are thoroughly dry (*5*). Continue the heating until the paper is black and all volatile matter is driven off (*6*). Push the lid slightly more to the side and heat the crucible more strongly, but do not bring the bottom of the crucible to more than a slightly red color (*7*). When all the paper has burned, place the crucible in a muffle furnace at 1000° for 30 min. Remove the crucible, allow it to cool below redness, place it in the desiccator and cover with the lid, and allow the desiccator to cool.

Measurement. Weigh the crucible (covered with the lid) as soon as it is cool (*8, 9*). Re-ignite the residue to constant weight. Calculate the percentage of calcium. The residue is calcium oxide, CaO.

Method II. Determination as the carbonate. Filter the solution through a porous-bottom crucible, transferring to the crucible as much of the precipitate as possible. Prepare a 0.1 per cent ammonium oxalate washing solution. Use it, at room temperature, to complete the transfer of the precipitate to the crucible, and to wash the precipitate until 1 ml of the last washings shows no test for chlorides (*4*). Dry the crucible and contents for 30 min. at 110°, transfer the crucible to a muffle furnace regulated for 525°, and heat for 1 hr.

Measurement. Cool the crucible in a desiccator and weigh. Repeat the heating until constant weight is obtained. Add three to four drops of a saturated solution of ammonium carbonate (*10*), dry for 30 min. at 110° to volatilize the excess ammonium carbonate, and weigh. Calculate the percentage of calcium. The residue is calcium carbonate, $CaCO_3$.

NOTES: (1) Otherwise some calcium carbonate may precipitate when the *p*H is adjusted to 6.

(2) Solutions of ammonium oxalate not freshly prepared may contain some carbonate which then gives calcium carbonate in the precipitate.

(3) Unfiltered ammonium hydroxide solution generally contains insoluble matter that could be weighed.

(4) Why test for chloride ion? How may the test be made in the presence of the oxalate ions?

(5) Too-rapid heating "fireproofs" the paper and thus makes a white residue difficult to obtain.

(6) In case some of the carbonaceous matter fractionally distills on the inside

of the cover, the deposit may volatilize completely only when the cover is removed and heated, upside down.

(7) The intensity of heating can be controlled easily by regulating the gas and air supplies to the burner, or by supporting the crucible on a ring about 15 cm above the burner, and then gradually lowering the ring.

(8) As carbon dioxide and water vapor are absorbed rapidly by the oxide, the required amount of weights (as nearly as possible) should be placed on the balance pan before the crucible is removed from the desiccator.

(9) The residue should not stand in a desiccator charged with calcium chloride for more than 45 min. before weighing. Calcium oxide is a more powerful dehydrating agent than calcium chloride.

(10) This treatment provides for reconversion of any partially decomposed calcium carbonate.

Exercise 28.6. Determination of Silicon in Steel

Silicon is found in steel and cast iron in one of several combinations. In any case, dissolution of the metal in an acid, e.g., nitric acid, converts the silicon to the quadrivalent state, with the formation of hydrous silicon dioxide. Following dissolution of the metal, perchloric acid is added to the solution, which is then evaporated to dehydrate the hydrous silica, $SiO_2 \cdot xH_2O$, before filtration.

A violent explosion may occur if organic matter comes into contact with fuming perchloric acid. The instructor's directions should be followed closely.

The Sample

Selection and preparation. Use drillings or cuttings representative of the material to be analyzed.

Measurement. Weigh to three decimal places a sample of about 2 g (*1*) and transfer it to a 400-ml beaker.

Treatment. Add 40 ml of 6 *M* nitric acid, cover the beaker, and allow the action to proceed until the metal is decomposed.

The Desired Constituent

Separation. Rinse the cover glass, add 40 ml of 60 per cent perchloric acid, and evaporate to fumes of this acid. Re-cover the beaker and boil gently (*2*) for 15 min., but without permitting the liquid to reach a pasty or solid state. After cooling the solution somewhat, add 100 ml of hot water and dissolve all soluble salts (*3*). Transfer the solution and residue to a paper filter, using hot 0.6 *M* hydrochloric acid. Wash with alternate portions of this solution and hot water until the residue is free

of iron (*4*). Ignite in a *platinum* crucible, with a very gradual rise of temperature until the paper is thoroughly charred.

Measurement. Weigh the residue of impure silica. Moisten it with 9 *M* sulfuric acid and pour about 5 ml of hydrofluoric acid (*5*) into the crucible. Volatilize the acids by heating in an air bath (*6*). Finally, ignite strongly to decompose any sulfate. Weigh the crucible again. The loss in weight is taken to be the silica. Calculate the percentage of silicon.

NOTES: (1) If a factor-weight sample is desired, how much should be taken?

(2) The boiling should be sufficient to cause the acid to condense and run down the wall of the beaker.

(3) Any lumps may be crushed with a stirring rod.

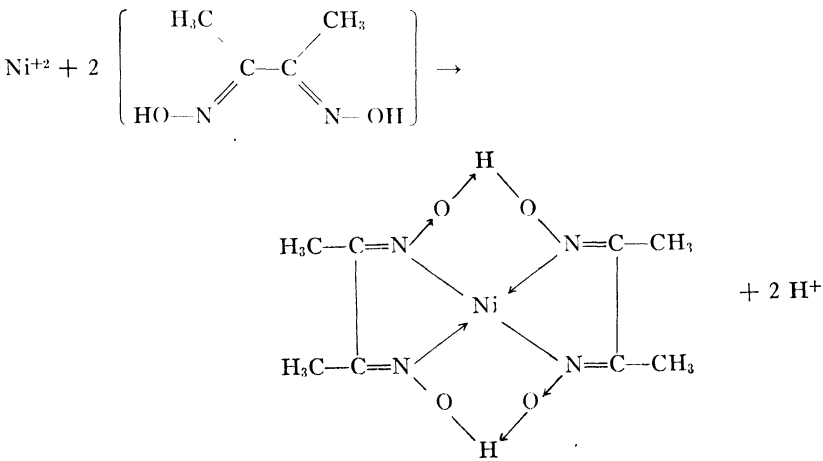
(4) If the perchloric acid is not completely removed, small explosions occur during ignition.

(5) Hydrofluoric acid must be handled with *caution* to avoid burns. Follow the instructor's directions.

(6) The platinum crucible may be placed inside a larger porcelain crucible.

Exercise 28.7. Determination of Nickel in Steel

One of the most frequently cited examples of the application of an organic precipitant is the use of dimethylglyoxime (2,3-butanedionedioxime) for the gravimetric determination of nickel in steel. A common formulation of the equation for the reaction is



The inner-complex compound formed is insoluble in an ammoniacal solution.[16] To prevent precipitation of the iron, a soluble complex is formed with tartaric acid.

[16] See Diehl, *Chem. Rev.* **21**, 39 (1939), for a discussion of the type of chelate complex represented by dimethylglyoxime.

Apparatus

Prepare a Gooch crucible, or use a fritted-bottom crucible of medium porosity. In either case, dry at 150°.

The Sample

Selection. Secure a representative sample of steel by making drillings or millings.

Measurement. Weigh accurately about 1 g of sample (*1*), transfer to a 400-ml beaker, and cover.

Treatment. Add 60 ml of hydrochloric acid (1:1) and warm to hasten dissolution (*2*). Add cautiously 10 ml of nitric acid (1:1). Boil, to oxidize any carbides and to expel brown oxides of nitrogen. Dilute to 200 ml with hot water.

Add 25 ml of 20 per cent tartaric acid (*3, 4*). Using litmus paper, neutralize the solution with concentrated ammonium hydroxide and add 1 ml in excess. Filter any insoluble material on paper and wash with hot water containing a little filtered ammonium hydroxide and ammonium chloride (*5*).

The Desired Constituent

Separation. Make the solution just acidic with hydrochloric acid and warm to about 70°. For each per cent of nickel present add 10 ml (*6*) of a 1 per cent ethanolic solution of dimethylglyoxime (*7*). Make slightly alkaline with ammonium hydroxide, digest for 30 min. at 60°, and cool to room temperature.

Filter on a Gooch or fritted-bottom crucible under mild suction. Keep the layer of precipitate wet until washing is completed with cold water.

Measurement. Dry the precipitate at 150° and weigh (*8*) as $Ni(C_4H_7O_2N_2)_2$.

NOTES: (1) If less than 3 or more than 5 per cent of nickel is known to be present, adjust the sample weight accordingly.

(2) Modifications for steels containing alloying elements in addition to nickel may be found in *Book of ASTM Methods for Chemical Analysis of Metals,* 1950, page 103.

(3) Dissolve 250 g of $C_4H_6O_6$ in 1000 ml of water.

(4) Tartaric acid forms soluble complexes with copper, chromium, iron, manganese, and vanadium, and thus prevents interference by these metals.

(5) Undissolved particles of carbon may be present. More likely, cloudiness indicates insoluble silicic and/or tungstic acids. In any such cases, high results would be obtained.

(6) If too much precipitant is used, dimethylglyoxime itself may appear, because

of its low solubility in water. It may be recognized by the light color of the crystals among those of the colored dimethylglyoxime-nickel complex.

(7) Dissolve 10 g of $C_4H_8O_2N_2$ in 1 liter of 95 per cent ethanol.

(8) Some analysts dissolve the precipitate at this point, electrodeposit the nickel and weigh it.

Exercise 28.8. Determination of Sodium and Potassium Indirectly[17]

By an *indirect analysis* is usually meant a procedure in which the desired constituent is not determined by a direct measurement (as in the titration of iron with dichromate or in the determination of chloride ion in the form of silver chloride).

There are a number of different kinds of procedures used in accomplishing determinations indirectly. In general, they all involve measuring some constituent in the sample which bears a known relationship to the desired constituent(s). Knowing this relationship, the analyst may then calculate the amount of the desired constituent. The numerical problems on page 661 illustrate some of these possibilities.

Such methods are scattered more or less throughout the analytical literature. To illustrate their application, the following typical cases have been selected as classes of examples:

1. An element or radical is determined which is known to be equivalent to the desired constituent. In the titrimetric determination of calcium with permanganate the oxalate ion titrated is assumed to be equivalent to the calcium. Similarly, in the titrimetric determination of copper with thiosulfate the iodine titrated is assumed to be equivalent to the copper.

Usually most writers do not refer to this kind of method as being indirect.

2. A noncommon element or radical is determined in a weighed mixture. In mixed iron and aluminum oxides, $Fe_2O_3 + Al_2O_3$, the iron may be determined titrimetrically or colorimetrically, and the aluminum then calculated. Similarly, in mixed alkali chlorides, $NaCl + KCl$, or mixed alkali sulfates, $Na_2SO_4 + K_2SO_4$, the potassium may be separated as $KClO_4$, $KB(C_6H_5)_4$, or K_2PtCl_6 and measured gravimetrically.

3. A common element or radical is determined in a weighed mixture. With the mixed alkali halides, $NaCl + KCl$, the chlorine may be determined gravimetrically or titrimetrically. For the corresponding mixed sulfates, $Na_2SO_4 + K_2SO_4$, the gravimetric method for sulfates is probably the most reliable.

4. A mixture containing two compounds having an element or radical

[17] As the gravimetric method for chloride is recommended here, the whole procedure is included with other gravimetric methods.

in common is converted to another mixture also containing an element or radical in common. An example of this type is the conversion of a weighed mixture of alkali chlorides, $NaCl + KCl$, to the sulfates, $Na_2SO_4 + K_2SO_4$, by heating with sulfuric acid at a temperature high enough to drive out the chlorine and the excess acid. The resulting sulfates are then weighed.

5. A weighed mixture is converted to a single compound. Thus, one may weigh a precipitate consisting of a mixture of silver bromide and silver iodide, $AgBr + AgI$. On chlorination, the mixture is converted to silver chloride:

$$(2\ AgBr + 2\ AgI) + 2\ Cl_2 \longrightarrow 4\ AgCl + Br_2\uparrow + I_2\uparrow$$

From the loss in weight the amounts of bromine and iodine may be calculated.

Many methods involving some kind of indirect measurement are possible for determining desired constituents. Those of the first type mentioned are most common. In general, they are all usually avoided, if possible, primarily because of the following objections:

1. Unless conditions are carefully controlled to compensate errors, the analyst may not be justified in assuming that the constituent measured is equivalent to the one desired. This possibility often accounts for the recommendation that a titrant be standardized under the working conditions for a given determination.

2. Any error in the determination of one constituent, as iron in the mixed oxides $Fe_2O_3 + Al_2O_3$, is inevitably attached also to the calculated amount of the other noncommon constituent (aluminum in this case). If one error is positive, the other is negative.

3. The large multiplying factors involved in some cases necessitate very careful measurements if the calculated quantities are to have reasonable reliability. Thus, the factors used in calculating sodium and potassium on conversion of the mixed chlorides $NaCl + KCl$ to the mixed sulfates $Na_2SO_4 + K_2SO_4$, render use of this otherwise attractive method very questionable.

Such situations are especially objectionable when there is much more of one desired constituent than of the other. A small measurement error may then result in a high percentage error for the constituent present in small amount.

The indirect method has long been used for determining sodium and potassium in many substances, such as water and limestone. Such applications usually necessitate involved separations of interfering constitu-

ents to obtain the mixed chlorides or sulfates of the alkalies. In order to shorten the procedure, the method described is designed for student samples containing sodium chloride, potassium chloride, and silica.

Since the determination is to be made indirectly, inspection of cases two, three, and four, mentioned already, indicates that this mixture may be handled by an adaptation of any one of three possibilities. If time is available, all of them may be tried and the results compared. Since the gravimetric determination of chloride is probably subject to least error, case three is recommended, using this method of measurement for the common constituent in the mixed alkali chlorides. Other possibilities are determination of the potassium gravimetrically, after separation as the perchlorate, the tetraphenyl borate, or the chloroplatinate, or determination of the chloride titrimetrically by means of silver nitrate.

The Sample

Selection. Use the sample provided by the instructor.

Measurement. Weigh accurately on a watch glass a 2-g portion of the dried sample and transfer to a 250-ml beaker.

Treatment. Add about 50 ml of water and heat nearly to boiling, to dissolve the sodium and potassium chlorides.

The Desired Constituents

Insoluble matter: Separation. Filter the solution through a Whatman No. 42 paper (*1*), catching the filtrate in a 250-ml volumetric flask. Transfer the insoluble material to the paper and wash well with hot water (*2*). Reserve the filtrate for the determination of chloride ion. Burn the paper in a porcelain crucible and ignite the residue at 900° to constant weight.

Measurement. Weigh the ignited insoluble material and calculate the percentage.

Chloride ion: Separation. The filtrate contains the sodium and potassium chlorides, their amount being the difference between the weights of the sample and of the insoluble material. Dilute this filtrate to 250 ml and mix well.

If there is less than 10 per cent of insoluble matter, transfer 25.00 ml of the filtrate to a 250-ml beaker. Otherwise use a 50.00-ml aliquot for this determination.

Precipitate the chloride ion with silver nitrate according to the directions given on page 478. Filter, wash, and dry as previously directed.

Measurement. Weigh the precipitate of silver chloride and calculate

the percentage of chlorine in the original sample (*3*). Then calculate the percentages of sodium and of potassium (*4*).

NOTES: (1) Other paper (e.g., Schleicher and Schüll, Blue Ribbon No. 589) or a Gooch crucible may be used.

(2) This separation is based on selective dissolution, the alkali chlorides being soluble and the silica insoluble in water.

(3) Account should be taken of the size of the aliquot of the filtrate used for determining chlorine.

(4) See problems on indirect methods, Chapter 33.

ELECTRODEPOSITION-GRAVIMETRIC METHODS

Although it has been found possible to separate many elements electrolytically,[18] the number of elements actually handled in this way in commercial laboratories is relatively small. Many separations that appeared attractive 30 years ago have been superseded by some other method.

Chapter 9 contains a brief presentation of the principles on which electrochemical separations are based. Included in the present section are directions for effecting the separation of several elements. The directions for the analysis of brass, in Chapter 31 also include the electrochemical separation of copper. Of all the elements, copper is probably the most often handled in this way. Other elements for which the electrolytic method is more or less frequently suggested are lead, cobalt, nickel, and silver. The details for each of these procedures involve some individual variations in composition of the electrolyte used and in certain other items.

Exercise 28.9. Determination of Copper in an Ore

Although copper may be deposited quantitatively, in adherent form, from a number of electrolytes, nitric or sulfuric acid solutions are usually recommended. Since the element deposits best from nitric acid, this solvent is preferable and is used whenever possible. In such solutions high voltages evolve hydrogen. The beneficial effect of the nitrate ion is said to depend upon its reaction in preference to the hydrogen ion, according to one or both of the equations

$$10\ H^+ + NO_3^- + 8\ e \rightarrow 3\ H_2O + NH_4^+$$
$$2\ H^+ + NO_3^- + 2\ e \rightarrow H_2O + NO_2^-$$

Since the nitrite ion hinders complete deposition, it is eliminated by urea, according to the equation

$$2\ H^+ + 2\ NO_2^- + CO(NH_2)_2 \rightarrow 3\ H_2O + CO_2\uparrow + 2\ N_2\uparrow$$

[18] Sand, *Gravimetric Electrolytic Analysis,* Blackie, 1940; Schleicher, *Elektroanalytische Schnellmethoden,* Enke, 1947; Smith, *Electro-Analysis,* Blakiston, 1918.

Sulfamic acid functions similarly,

$$HOSO_2NH_2 + HNO_2 \rightarrow H_2SO_4 + N_2\uparrow + H_2O$$

The directions given below for a copper ore provide for various complications arising from the presence of interfering constituents. For samples in which these are known to be absent the procedure may be correspondingly simplified.

The procedure suggested for displacing copper by means of aluminum illustrates a separation accomplished by electrochemical reduction without external current. The process provides for the interference of elements having decomposition potentials near that of copper, e.g., antimony, arsenic, bismuth, mercury, and silver.

The Sample

Selection and preparation. Select representative portions of the material to be analyzed.

Measurement. Weigh two samples of about 0.5 g of ore each, and transfer to casseroles.

Treatment. To each sample add a mixture of 5 ml of concentrated nitric acid and 10 ml of concentrated hydrochloric acid and boil gently for 15 to 20 min. to hasten dissolution. Place the casserole on the steam hot plate until action ceases.

The Desired Constituent

Separation of lead and gangue. Add 7 ml of concentrated sulfuric acid and evaporate to fumes of sulfur trioxide, by swirling the solution in a casserole over a free flame or by using a heater above the surface of the solution. Cool the solution, add 25 ml of water, and boil to dissolve soluble salts. Filter to remove gangue and lead sulfate. If the displacement separation from interfering metals must be made, receive the filtrate in a casserole. Otherwise use a 200-ml tall-form beaker. Wash the residue well with hot water.

Separation of copper from interfering constituents. Dilute the filtrate in the casserole to about 75 ml. Place in the solution a piece of clean, heavy sheet aluminum (*1*) about 2×15 cm, bent into circular form. Boil the solution gently to displace the copper (*2*). Allow the solution to cool somewhat and then filter quickly, using hydrogen sulfide water (*3*) as a washing medium to rinse out the beaker and to transfer to the paper any loose particles of copper. Wash with the hydrogen sulfide solution and discard the filtrate, which should be clear. By means of 10 ml of 1:1

nitric acid dissolve the copper adhering to the aluminum in the casserole. Place a 200-ml tall-form beaker under the funnel and transfer the solution in the casserole to the funnel to dissolve the copper there. Puncture the paper and wash thoroughly with hot water. Boil the solution to remove oxides of nitrogen. To prevent possible incomplete deposition from nitric acid solution, add one drop of 0.1 *N* hydrochloric acid.

Separation of copper. Place clean platinum electrodes (*4*) in the beaker, support it on blocks about 3 in. above the table top, and connect the electrodes to a source of current, making the gauze electrode the cathode. The latter should have its lower edge close to the bottom of the beaker (*5*). Add 1 g of ammonium nitrate, stir, add water to bring the solution to within 6 to 8 mm of the top of the cathode, and cover with a split watch glass. Connect the two electrolysis cells, placed in series, to a source of direct current that will furnish at least 6 volts. Set the adjustable resistance so that a visible film of copper is deposited within 5 min. (*6*). When the deposit is well started, increase the rate gradually, keeping in mind only that the copper should be bright and adhere to the electrode.

After the color of the cupric ion disappears, add 0.5 g of urea and allow the electrolysis to proceed 30 min. longer. Add water to bring the solution to the top of the cathode, stir, and electrolyze for another 15 min. If no copper appears on the freshly exposed platinum (*7*), rinse off the cover glass. Holding the beaker in one hand, remove the supporting blocks. Then slowly lower the beaker, and wash the exposed cathode with a stream of water from a wash bottle (*8*). As soon as the cathode is above the surface of the solution, remove the electrode, rinse in ethanol, and dry on the steam hot plate (*9*). If two separations are being run in series, connect the circuit through the second as soon as that through both is broken, and electrolyze 15 min. more.

Measurement. Weigh the cathode with the deposit of copper. Dissolve the copper by heating in hot, dilute nitric acid. Rinse the electrode in water, dry, and reweigh. The difference in weight is the copper deposited (*10*). Calculate the percentage of copper.

NOTES: (1) Stock of about 20 gauge is convenient to use.

(2) The solution should be colorless unless enough ferrous sulfate to give a greenish hue is present. Failure to expel completely the nitric acid during volatilization will prevent complete removal of the copper.

(3) Using hydrogen sulfide water will cause any copper in solution to precipitate.

(4) Greasy fingerprints on electrodes prevent the formation of uniform deposits.

(5) If the electrode does not reach the bottom of the beaker, the solution should be stirred occasionally to insure separation of copper from the bottom layer. This difficulty does not arise with the use of stirring by air or other means.

(6) A voltage must be applied somewhat in excess of the decomposition potential of the solution being electrolyzed. This value varies with the concentration and nature of the solution. Too-rapid deposition produces unsatisfactory, non-adherent deposits.

(7) This test for completion of deposition may be confirmed by removing a few drops of solution from the bottom of the beaker (with a pipet) and testing with potassium ferrocyanide. A brown precipitate or reddish coloration indicates copper.

(8) Washing deposits of copper should be done quickly and with special care to prevent dissolution of the metal in any nitric acid not washed off. If the solution is not to be used for subsequent determinations, the safest procedure is to remove it from the beaker by means of a small siphon, the level of the solution in the beaker being maintained by addition of water. Complete removal of the electrolyte is shown when the ammeter needle drops to zero.

(9) The deposit may be immersed in a beaker of 95 per cent ethanol and dried 2 to 3 min. in an oven at 105°.

(10) Use of this method prevents difficulties arising from a possible slight change in weight of the electrode through transfer of platinum from anode to cathode.[19] Most authors do not deem this precaution necessary, and simply weigh the electrode before and after deposition.

Exercise 28.10. Determination of Copper and Silver in an Alloy

The determination of silver and copper in sterling silver or coinage silver[20] serves as a good illustration of the application of the electrolytic method of separation. The sample is first dissolved in nitric acid and is then evaporated to remove the excess acid. From a solution of the complex cyanides $KAg(CN)_2$ and $K_2Cu(CN)_3$, the silver is deposited, with controlled voltage. After the remaining solution is acidified with nitric acid and hydrocyanic acid boiled out, the copper is deposited.

The Sample

Selection and preparation. If the alloy is not clean, wash it with some liquid, such as acetone or dilute ammonium hydroxide, that will not dissolve any of the metal. Use the whole piece if a coin is to be analyzed, or drillings or cut pieces if the sample is some other alloy.

Measurement. Weigh about 0.5 g of sample (*1*) and transfer to a casserole.

Treatment. Cover the casserole and add 10 ml of 1:1 nitric acid. Raise the cover glass on hooks and evaporate the solution just to dryness on the steam hot plate (*2*). Dissolve the residue in 10 ml of water (*3*)

[19] Kelly and Molloy, *J. Am. Chem. Soc.* **53**, 1337 (1931).

[20] For application to silver solders, see Miller, *Ind. Eng. Chem., Anal. Ed.* **8**, 431 (1936).

and transfer to a 200-ml tall-form beaker containing 20 ml of 10 per cent potassium cyanide (*4*) solution (*5*).

The Desired Constituents

Separation of silver. Place the electrodes in the beaker, set the beaker on blocks above the table top, connect the electrodes to the source of current, and dilute the solution to cover the cathode. Start the electrolysis at 0.1 amp. (*6*). If the deposit is forming satisfactorily, the amperage may be raised gradually until the voltage reaches 1.5 (*7*). When the deposition of silver is complete (*8*), remove the blocks supporting the beaker and lower it slowly, washing the cathode well with a stream of water. When the solution has dropped below the cathode, remove the electrode and wash it thoroughly. If checking determinations are to be made, remove the second electrode. Dry the deposit at 105°.

Measurement. Weigh the deposit of silver, dissolve it in dilute nitric acid, dry the electrode, and reweigh. Calculate the percentage of silver.

Separation and measurement of copper. Add 5 ml of concentrated nitric acid (*in a hood*) (*6*) to the solution from which silver was deposited. Boil the solution gently for 15 min. to expel hydrogen cyanide. Electrolyze the solution for copper according to the directions given previously for this element.

NOTES: (1) If a whole coin is used, the solution may be diluted to a definite volume and an aliquot portion taken.

(2) The nitrates should not be decomposed by baking on a hot plate.

(3) Any insoluble brown residue of gold may be disregarded.

(4) Potassium cyanide of analytical quality should be used.

(5) Silver deposits best from a solution in which it is dissolved as the complex cyanide $Ag(CN)_2^-$. The deposit is white and adherent, but lusterless. The fact that the metal can be deposited from such a solution indicates that there must be some silver ions present, presumably from the ionization of the complex

$$Ag(CN)_2^- \rightleftarrows Ag^+ + 2\ CN^-$$

(6) Do not inhale the gases evolved from the electrolytic cell. *Never handle cyanide solutions in a pipet*, as they are extremely poisonous.

(7) High-current density promotes decomposition of potassium cyanide around the anode, resulting in a darkening of the solution. Mixing and diffusion may carry the product to the cathode and darken the silver.

(8) To test for silver, transfer a few drops of the electrolyte to a test tube, make just acidic with dilute hydrochloric acid, and boil out hydrogen cyanide (*under a hood*).

Exercise 28.11. Analysis of a Copper-Nickel Alloy

A number of alloys, including monel metal and certain coinage alloys, are composed principally of copper and nickel. A small amount of iron

is often found to be associated with these two elements. The procedure described below illustrates the application of the electrolytic method of separation in the analysis of such an alloy for its major constituents, copper and nickel. If iron is present, it may be separated by precipitation, following a volatilization separation of the nitrate ion.

The Sample

Selection and preparation. If the alloy is not clean, wash it with dilute ammonia or acetone, and then with water. After drying the alloy, secure by suitable means representative portions for the sample.

Measurement. Weigh a sample of 0.3 to 0.5 g and transfer to a 200-ml tall-form beaker.

Treatment. To dissolve the sample, add 15 ml of an acid mixture consisting of water, concentrated sulfuric acid, and concentrated nitric acid in a 10:1:2 ratio. When dissolution is complete, boil out the oxides of nitrogen.

The Desired Constituents

Separation of copper. Proceed with the separation and measurement of copper as directed for the determination of copper in Exercise 28.9. Keep the voltage below 2.7. Set the solution aside for subsequent determinations.

Separation of iron. Set the beaker on the steam hot plate, raise the watch glass on hooks and evaporate the solution as far as possible. Continue the evaporation by raising the temperature and heating until sulfur trioxide fumes appear (*1*). This raising of temperature may be accomplished by use of an infrared heating lamp placed above the surface of the solution, or by holding the beaker in tongs over a low flame and swirling the solution. To the cool solution add 25 ml of water. Now heat the solution and add enough filtered ammonium hydroxide to precipitate the iron and to convert the nickel to the blue complex ion $Ni(NH_3)_4^{+2}$. Transfer the precipitate to a paper filter, catching the filtrate in a tall-form beaker. After washing the precipitate several times with hot water, place the original beaker under the funnel, dissolve the precipitate in 5 ml of dilute sulfuric acid, and wash the paper well. Reprecipitate the iron with ammonium hydroxide (*2*). Filter on paper, allowing the filtrate to run into the beaker containing the main portion of the nickel. Wash well with water (*3*).

Dissolve the precipitate on the filter paper with 1 to 2 ml of oxalic acid solution saturated at room temperature. Wash the paper with hot water,

catching the solution in a tall-form beaker containing 5 gm of ammonium oxalate in 50 ml of water (*4*). Place the electrodes in the beaker, dilute to bring the solution to the top of the cathode, and electrolyze the complex oxalate, starting the deposition at 1 amp. (*5*). When the deposition is thought to be complete (*6*), test a drop of the electrolyte with potassium ferricyanide. If no iron is detected, lower the beaker slowly and wash the cathode as the solution drops. Remove the cathode, rinse at once in ethanol (*7*), and dry at 105°.

Measurement. Weigh the deposit and dissolve the iron in hot, dilute sulfuric acid. Calculate the percentage of iron.

Separation of nickel. To the filtrate from the iron add 15 ml of concentrated ammonium hydroxide. Place the electrodes in the beaker, connect them to the source of current, and dilute the solution with water until the gauze cathode is just covered. With stationary electrodes, start the electrolysis at 0.5 amp. If at the end of 15 min. the nickel is depositing satisfactorily (*8*) raise the current to 1 amp. The disappearance of the blue hue of the complex ion $Ni(NH_3)_4^{+2}$ indicates the depletion of the nickel. After an additional 15 min., test a drop of the solution from the bottom of the beaker with dimethylglyoxime. When deposition is complete, wash the deposit well with water while lowering the beaker slowly. Dry the deposit at 105°.

Measurement. Weigh the electrode with the deposited nickel. Dissolve the deposit by boiling the electrode in concentrated nitric acid for at least 15 min. (*9*). Wash and dry the electrode and reweigh. Calculate the percentage of nickel.

NOTES: (1) Nickel does not deposit best from a solution containing nitrate ions. The evaporation serves also to oxidize any reduced iron.

(2) The separation of iron is not entirely complete at this point.

(3) Instead of making an electrolytic separation of the iron, the precipitate of the hydrous oxide may be transferred to a crucible and ignited to ferric oxide, as in the analysis of limestone. Alternatively, the iron may be determined colorimetrically (see Chapter 29).

(4) Iron deposits best from a complex oxalate solution.

(5) The decomposition voltage is approximately 2, disregarding overvoltage effects.

(6) Some solutions deposit little or no iron under these conditions, but immense volumes of hydrogen are evolved at the cathode. Occasionally, the initial deposition of iron seems to be aided by tapping the cathode to prevent the excessive amounts of gas bubbles from covering the entire surface.

(7) Iron oxidizes relatively rapidly.

(8) Deposits of nickel are often obtained that can hardly be distinguished from the platinum of the electrode.

(9) Care must be exercised to get all the nickel dissolved.

EXTRACTION-GRAVIMETRIC METHODS [21]

In Chapter 10 an outline of the general principles underlying the accomplishment of quantitative separations by means of extraction methods was presented. As noted there, the process may be adapted to samples in the solid, liquid, or gaseous state.

The exercises described below will serve as examples of the application of the principle of extraction to separate a desired constituent from a solid and a liquid. Measuring the constituent by weight justifies the designation of extraction-gravimetric method in these cases.

Exercise 28.12. Determination of Fat in Milk

The Roese-Gottlieb extraction-gravimetric method for determining fat may be applied both to whole, skim, and condensed milk and to milk powder. The extraction must be preceded by treatment of the sample with ethanol and ammonium hydroxide in order to secure all the fat.

The Sample

Selection and preparation. The milk or milk product to be analyzed should be handled to secure a representative sample for the determination.

Measurement. With a pipet, transfer 10 ml of milk to a Rohrig tube (Figure 28.10).

Treatment. Add 1.25 ml (*1*) of concentrated ammonium hydroxide, stopper the tube and invert it to mix the contents. Then add 10 ml of 95 per cent ethanol and mix again.

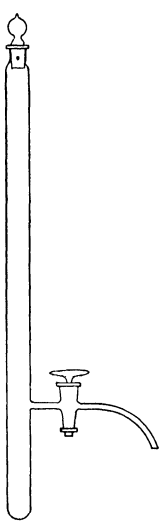


Figure 28.10
Rohrig tube.

The Desired Constituent

Separation. To extract the fat, add 25 ml of diethyl ether, stopper the tube and shake for 1 min. Then add 25 ml of petroleum ether (*2*) and shake for the same length of time. After standing, both layers of liquid should be free of suspended matter and the lower layer of air bubbles. The ethereal solution of the fat in the upper layer is drawn off through the side tube as completely as possible without removing any of the lower layer. To insure absence of suspended particles, the ethereal solution should be withdrawn into a small, dry, paper filter and allowed to run into a dry, weighed, fat flask. To render the extraction more nearly complete,

[21] See Assoc. Offic. Agr. Chemists, *Methods of Analysis*, p. 233, 1950.

treat the sample again in the same way, using 15 ml of each ether. Wash the outlet tip and the filter with some of the extraction mixture. Then evaporate the solvent on a steam hot plate (*3*) and dry the flask at 100°.

Measurement. Weigh the fat extracted and calculate its percentage (*4*).

NOTES: (1) Use 2.0 ml for sour milk.

(2) The petroleum ether should be a product distilling below 65°.

(3) Low-boiling solvents should be kept away from open flames.

(4) By what must the volume of sample be multiplied to obtain the weight of sample in grams?

Exercise 28.13. Determination of Crude Fat in Peanuts

Many foods contain considerable amounts of fats, which are glycerides of acids (e.g., oleic, palmitic, and stearic). These constituents, in addition to various other substances, such as wax resin and certain coloring matters, may be extracted by the described process. The result should be designated as ether extract or crude fat.

The Sample

Selection and preparation. Select an appropriate number of peanuts representative of the batch to be analyzed. Shell the peanuts, discarding the husk and brown skin. Slice the seeds with a knife and then crush the pieces in an agate mortar until they are free of lumps (*1*).

Measurement. Weigh a sample of about 2 g into a dry weighing bottle.

The Desired Constituent

Separation of moisture. Place the bottle containing the sample in an oven at a temperature of 105° for an hour (*2*). If the percentage of the water is desired, the bottle may be reweighed and the loss calculated.

Separation of fat. Transfer the dried sample to an extraction thimble of paper or alundum and cover with a half-inch layer of ether-extracted cotton. Place the thimble in an extraction tube of the continuous or intermittent type (see Chapter 10). Transfer 35 ml of pure, dry, diethyl ether (*3*) to a dry, weighed, fat flask of 125-ml capacity and connect to the extraction tube. Put the vertical condenser in place and start the cooling water through it. Turn on the current to the electric heater, interposing a sheet of asbestos paper between the flask and the heater if the rate of boiling of the ether is too fast. The condensed ether should

drop inside the extraction thimble. Allow the extraction to proceed for 3 hrs.

Turn off the heater and allow the extraction tube to drain for 15 min.; or disconnect the extraction tube and flask from the condenser, remove from the heating element, and allow to drain 5 min. Then remove the flask and allow the ether to evaporate under a hood, or recover it by connecting to a condenser and distilling into a suitable container. When about 2 ml of liquid remains in the flask, remove the latter and volatilize the remaining ether by directing a stream of hot air into the flask.

Measurement. After cooling the flask, weigh it and calculate the percentage of fat (*4*).

NOTES: (1) The seeds cannot be ground in a mill on account of the amount and nature of the fat. Crushing in a mortar produces a sticky mess.

(2) The extraction cannot be accomplished successfully if the sample contains an appreciable amount of moisture. Therefore, the moisture should be removed by dehydration at 105°.

(3) To remove alcohol from commercial ether, shake with water in a separatory funnel. Remove the upper, ethereal layer and add solid, anhydrous calcium chloride to it. Discard the resulting aqueous layer. To the residual ether add clean sodium wire and distill off the ether.

(4) If the amount of moisture was determined, the percentage of fat may be reported for both the dried and moist sample.

CHAPTER 29

COLORIMETRIC METHODS[1]

For many decades titrimetric and gravimetric methods have been the two best known and most widely used general procedures of quantitative chemical analysis. Some writers refer to them as the classical methods. During the last two decades, however, colorimetric methods have acquired an important place in the laboratories of industry, public welfare centers, and research organizations. The procedures included in this chapter were selected as an introduction to this kind of method.

To illustrate several different kinds of instruments, the directions in particular cases specify a standard series comparimeter, a Duboscq balancing instrument, a filter photometer, and a spectrophotometer. It should not be assumed that the particular instrument mentioned is the only one that can be used in the given case. Except in special cases, not considered here, such instruments are usually interchangeable, if adequately checked against suitable standards.

The particular procedures described were selected to illustrate different points in colorimetric work. The following items are perhaps most important: (1) the use of several different kinds of reagents and reactions for developing colors; (2) the use of three different colored heteropoly systems for handling a non-metal, phosphorus; (3) the use of a half dozen absorptimetric methods for determining as many constituents in a single type of material, a magnesium-base alloy; and (4) the use of several systems to show how different experimental methods may yield different data for the same substance.

Exercise 29.1. Determination of *p*H

The colorimetric method for the determination of *p*H of solutions is not only one of the simplest of such procedures, but also it is one of the

[1] See Chapter 17 for a general discussion of this subject.

most widely used. The process is based on the action of certain indicator compounds that exhibit definite hues in solutions of given *p*H values.[2]

One method of applying this procedure consists in adding a definite amount of the indicator solution to a definite volume of each of a series of solutions of known *p*H values. The systems usually used for this purpose are standard buffer solutions. The same volume of unknown solution, in a tube of the same dimensions, is then treated with the same amount of indicator, and the unknown solution is compared with the known in order to find a color match. The process is known as a "standard-series comparison." Test tubes are often used for this purpose. A commercial comparimeter is illustrated in Figure 17.3 (page 257).

The useful indicators are the same type as those used for determining end points in neutralization titrations. The list of indicators given in Table 29.1 is useful in general work.

TABLE 29.1

SELECTED INDICATORS

Common Name	*pH Range*	*Color Change*	p*K*	*Concentration* (per cent)
Thymol blue	1.2- 2.8	red-yellow	1.7	0.008
Brom phenol blue	3.0- 4.6	yellow-lavender	3.9	0.008
Brom cresol green	3.8- 5.4	yellow-blue	4 7	0.008
Brom cresol purple	5.2- 6.8	yellow-purple	6 1	0.012
Brom thymol blue	6.0- 7.6	yellow-blue	7 1	0.008
Phenol red	6.8- 8.4	yellow-red	7.8	0.004
Cresol red	7.2- 8.8	yellow red	8.3	0.008
Thymol blue	8.0- 9.6	yellow-blue	8.9	0.008
Thymolphthalein	9.3-10.5	colorless-blue	9.8	0.008

The student will note that each indicator covers only a limited *p*H range. The particular one selected for a given case must include the *p*H of the unknown to be measured. This selection may require some preliminary testing. Thus, a solution that is blue to brom thymol blue may have a *p*H anywhere above (approximately) 7.4. If it is yellow with this indicator, the *p*H may be anywhere below (approximately) 6.2.

The most reliable method to follow requires the preparation of a series of buffer solutions having *p*H values 0.2 *p*H units apart, as described in

[2] See Clark, *Determination of Hydrogen Ions,* Williams and Wilkins, 1923; Britton, *Hydrogen Ions,* Van Nostrand, 1942; Kolthoff and Rosenblum, *Acid-Base Indicators,* Macmillan, 1937; Kolthoff and Laitinen, *pH and Electro-titrations,* Wiley, 1944; and Ricci, *Hydrogen Ion Concentration,* Princeton University Press, 1952.

the references cited. This method involves considerable work to prepare all the solutions.

In order to illustrate this general kind of method, Gillespie's[3] method is described. This "milliliter ratio" modification of the longer procedure has the great advantage of eliminating the buffer solutions. Although the results obtained may not be as reliable as with the use of carefully prepared buffer solutions, the method is satisfactory for some purposes. The same kind of comparison may be accomplished more elegantly by means of the Bausch and Lomb two-color modification of the Duboscq comparimeter.

Apparatus

A test-tube holder similar to that illustrated in Figure 29.1 should be available. Select enough test-tubes to fill both rows of holes in the block. They should have a diameter that is uniform and such that the tubes will just fit into the holes in the block. Clean the tubes and place one in each hole in the holder.

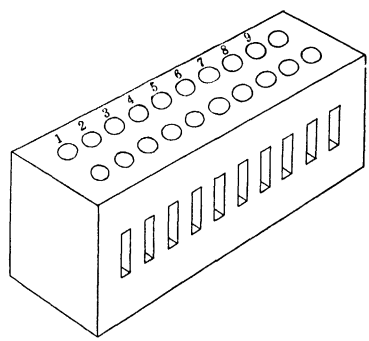


Figure 29.1

Test tube holder.

The Sample

Selection. The solution to be tested should be mixed and free of color and suspended matter.

Measurement. Transfer to a clean test tube 10 ml of the solution.

The Desired Constituent

Measurement. Determine the approximate *p*H of the solution by adding a few drops of several of the indicators listed in Table 29.1 to other separate portions of the solution (*1*). Having located an approximate value, select the indicator the *p*H range of which covers this value.

Prepare the standard series solutions in the tubes in the special holder (Figure 29.1). In the back row, by means of a 1-ml measuring pipet, place 0.15 ml of the indicator in tube 1, 0.20 ml in tube 2, 0.30 ml in tube 3, 0.40 ml in tube 4, 0.50 ml in tube 5, 0.60 ml in tube 6, 0.70 ml in tube 7, 0.80 ml in tube 8, and 0.85 ml in tube 9. Reverse the order in the front row by beginning with 0.85 ml in tube 1. Then all pairs of tubes, such as tubes 3 in the two rows, contain the same total amount of indicator. Now

[3] *J. Am. Chem. Soc.* **42**, 742 (1920).

add exactly 10 ml of a suitable acidic solution (*2*) to each tube in the back row. Similarly, add the same volume of a suitable basic solution (*3*) to each tube in the front row. Mix each solution.

The color observed on looking through any pair of tubes will be the result of a given amount of indicator being in the acidic form and a given amount being in the basic form. To the unknown solution should be added 1 ml of the indicator used. A test-tube containing only distilled water should be placed in front of the tube containing the unknown, in order that the unknown solution may be observed through the same total thickness of liquid as is found in the double row of standards. The unknown is then compared with the standard series to locate the matching pair.

The *p*H is calculated as follows:

$$p\text{H} = p\text{K} + \log \frac{\text{ml in basic form}}{\text{ml in acidic form}}$$

The *p*K values for the indicators are given in Table 29.1. One may simply add to or subtract from the *p*K value of the indicator the increment shown in Table 29.2 for the milliliter-ratio in the tube pair found to match.

TABLE 29.2

INDICATOR MILLILITER-RATIO RELATIONSHIPS

Solution	*Ml-ratio*	*Per Cent Neutralized*	*Increment to* p*K Value*
1	0.15/0.85	13.7	−0.8
2	0.20/0.80	20.0	−0.6
3	0.30/0.70	28.5	−0.4
4	0.40/0.60	38.7	−0.2
5	0.50/0.50	50.0	0.0
6	0.60/0.40	61.3	+0.2
7	0.70/0.30	71.6	+0.4
8	0.80/0.20	80.0	+0.6
9	0.85/0.15	86.3	+0.8

NOTES: (1) Use of one of the commercially available "universal indicators" facilitates locating the approximate *p*H.

(2) For the acidic colors, use 1.0 *N* acetic acid for bromphenol blue and bromcresol green, and 0.7 per cent KH_2PO_4 for the other indicators.

(3) For the basic colors, use a solution containing 18 g of $Na_2HPO_4 \cdot 12\ H_2O$ per liter for the bromphenol blue, bromcresol green, bromcresol purple, and bromthymol blue, and a solution containing 1.0 g of Na_2CO_3 per liter for phenol red, cresol red, and thymol blue.

Exercise 29.2. Determination of Manganese in Steel

A widely used method for determining manganese colorimetrically is based on oxidation of the manganous ion Mn^{+2} to the permanganate ion MnO_4^-. Periodate is used as an oxidant, the reaction being

$$2\ Mn^{+2} + 5\ IO_4^- + 3\ H_2O \rightarrow 2\ MnO_4^- + 5\ IO_3^- + 6\ H^+$$

The oxidation is accomplished in a hot, strongly acidic solution. Preferably, the concentration of the manganese should not exceed 2 mg per 100 ml of solution.

Since the major element in steel is iron, there is strong color interference by the ferric ion Fe^{+3}. Addition of phosphoric acid eliminates this interference through the formation of a colorless iron-phosphate complex. In alloy steels containing nickel and/or chromium interference by these elements occurs. Correction may be made by adding about the same amount of each to the standard as is contained in the unknown. Reference works on steel analysis should be consulted for details on interferences.

Apparatus

In order to illustrate the principle of the balancing type of comparimeter, a Duboscq instrument is suggested for this determination. A schematic diagram of the optics is shown in Figure 17.4 (page 258). An instrument with 10-cm cells is most convenient in this case.

The Sample

Selection. Procure drillings or millings representative of the steel to be analyzed (*1*).

Measurement. Weigh 0.5 to 1.0 g of sample and transfer it to a 250-ml conical flask.

Treatment. Dissolve the steel by heating with 70 ml of nitric acid (1:3) and boil for 1 min. Remove the flask from the burner and add 0.5 to 1.0 g of ammonium peroxydisulfate (persulfate) $(NH_4)_2S_2O_8$. Add a dozen glass beads and boil the solution for 10 to 15 min. to oxidize compounds of carbon and to destroy the excess oxidant. If any permanganate color develops, or if oxides of manganese appear, add a few drops of sulfurous acid to clear the solution. Then boil for a few minutes to expel oxides of nitrogen and sulfur.

Adjust the volume of solution to about 100 ml, add 25 ml of 6 *M* phosphoric acid and 0.5 g of potassium periodate, and boil for 5 min. (*2*).

Cool the solution, transfer it to a 250-ml volumetric flask, dilute to the mark, and mix well.

The Desired Constituent

Measurement. Clean the glass plungers and cells of the Duboscq instrument with water. Then either wipe them dry with cleaning tissue or rinse them with the solution to be measured. Also wipe any dust from the mirror, and adjust its angle to obtain the most satisfactory indirect light.

To check the instrument, put some of the standard colored solution (*3*) in each cup and set for a depth of 30 mm. Then move the other cup up and down, approaching and passing repeatedly the match point of color intensity. Gradually narrow the range covered until the point of exact match is obtained. The right-hand cup should then read 30 mm also. Should this not be the case, consult the instructor. Professional aid may be needed.

Empty one of the cups, rinse with the unknown solution, and then fill half-full with the unknown solution. Put in the other cup about the same amount of a standard solution of manganese prepared similarly (*3, 4*). Set the plunger in the known solution at a definite depth of solution and then adjust the plunger in the unknown until a color match is obtained. Repeat the setting twice and average the three readings.

The concentration of the unknown, C_u, is calculated as follows:

$$C_u = C_s \times \frac{b_s}{b_u}$$

where C_u = concentration of the unknown solution, C_s = concentration of the standard solution, b_s = depth of the standard solution, and b_u = depth of the unknown solution. Such a calculation rests upon conformity of the solution to Beer's law (*5*).

NOTES: (1) The procedure described is designed for plain carbon steels.

(2) Each 0.1 g of manganese requires about 1 g of potassium periodate.

(3) N.B.S. analyzed steels are excellent for this purpose. A standard manganous sulfate solution may be prepared by reducing a measured volume of standard permanganate solution with sulfur dioxide, boiling out the excess dioxide, and diluting to give a manganese concentration of 0.1 mg per ml.

(4) The standard, containing an excess of periodate, is stable for at least 3 months in a stoppered flask.

(5) The more closely the depth of the unknown approximates that of the standard, the more likely are the results to be accurate. Suitable dilution of standard or unknown will aid in achieving this result. See Chapter 17 for a discussion of this method of avoiding errors with systems not conforming to Beer's law.

Exercise 29.3. Demonstration of the Importance of Various Operational and Instrumental Details with Photometers

Most of the subsequent determinations may be made by means of standard series or balancing technics, often with very simple equipment. However, the use of filter photometers and spectrophotometers is recommended in Procedures 4, 5, and 6 in order to give the student additional instrumental experience.

These more complicated instruments may yield different transmittance values for some systems, depending on the type of instrument or the way in which it is used. The accompanying exercises provide demonstrations of several important variable factors.[4]

Instruments

Either visual or photoelectric instruments may be used in most cases. All visual equipment is subject to the difficulty of making reliable observations below 430 mμ or above 680 mμ. An additional difficulty is that slit-width control is not equally satisfactory on all spectrophotometers.

Because of their current prevalence, photoelectric instruments will be assumed to be used. Operating instructions should be available for each individual instrument.

In measuring of solutions, the absorption cell(s) should be carefully cleaned and then rinsed with some of the solution to be measured. After the cell(s) is filled to the necessary position, the outside faces through which the light beam passes should be wiped dry and clean with absorbent tissue.

Unless otherwise specified, 1-cm cells are assumed.

Materials

Certain colored glasses are excellent for demonstrating the relationship of spectrophotometric curve-form to the wavelength intervals at which readings are taken. Likewise, they serve to show the effect of the kind and number of filters used with a filter photometer, and also the significance of slit width in spectrophotometers. Corning didymium (No. 5120, 3-mm) and uranium (No. 9830, 2-mm) glasses are recommended.

Potassium permanganate is one of the best soluble substances to use for such a study. A convenient temporary stock solution (0.050 mg of manganese per ml) can be prepared by directly weighing 0.1440 g of $KMnO_4$, dissolving in water, and diluting to 1 liter. However, if the

[4] See Mellon, Chapter 6 in *Colorimetry for Chemists*, G. F. Smith Chemical Co., Columbus, O., 1945, for additional exercises, especially those dealing with variables involved in the solution.

solution is to be preserved, it should be prepared and standardized in the usual way.

Instrumental Variables

Photometric data, in the form of curves, may be presented in several ways, the one used depending upon the nature of the readings and the purpose for which the data are obtained. Most frequently the ordinate values are transmittancy (in per cent) and the abscissa values are wavelength (in millimicrons). If other types of data are desired, they may be calculated (see Chapter 17); some instruments are graduated to give such values directly.

Effect of concentration. Prepare 50 ml each of a series of permanganate solutions containing 50, 35, 20, 10, 5, 2.5, 1.0, and 0.5 mg of manganese per liter. With the spectrophotometer set for a definite spectral-band width, such as 10 mμ, determine the transmittancy-wave length curve for each solution by taking transmittancy readings at intervals of 10 mμ from 400 to 700 mμ.

Plot the series of curves with transmittancy (T_s) as ordinate, and wavelength (mμ) as abscissa, as shown in Figure 17.16 (page 271). For one of the intermediate concentrations use the same readings to plot another curve on semilogarithmic paper (log scale for the ordinate). Repeat this curve by plotting as ordinates the absorbancy values ($A = \log 1/T_s$) on a linear scale. Still another curve may be plotted by using values of log A as ordinates on a linear scale. On one of these plots mark the abscissa in both wave-length and frequency (3×10^5/wave-length, in mμ).

Effect of cell thickness. Using one of the more dilute solutions, e.g., 5 mg per liter, determine the transmittancy in cells of different thicknesses, such as 0.5, 1.0, 2.0, 5.0, and 10.0 cm at intervals of 10 mμ.

Plot the data in the form of transmittancy-wavelength curves to determine the optimum thickness of cell for this concentration (that is, the thickness that gives a transmittance of 30 to 40 per cent at the peak of the absorption band, which in this case is 525 mμ).

Effect of width of spectral band. Between 480 and 600 mμ determine the transmittancy of the permanganate solution containing 10 mg of manganese per liter for different spectral band widths, preferably 1.0, 2.5, 5.0, 10.0, and 20.0 mμ, if this is instrumentally possible. Take the readings at intervals of 5 mμ.

Plot the data as transmittancy-wavelength curves and note the differences, especially between 520 and 550 mμ.

This effect of band width may be illustrated in filter photometers by using different series of filters that may be available. The following possibilities are most likely: plain glasses, composite glasses, and interference-type glasses. The band of light passed decreases in width in this order.

Effect of wavelength intervals. Determine the transmittancy of the permanganate solution containing 20 mg of manganese per liter at a spectral-band width of 10 mμ (or less), the readings being taken at intervals of 10 mμ from 400 to 700 mμ.

Plot three separate smooth curves (on the same sheet) in the form of transmittancy-wavelength graphs by using the readings at intervals of 10, 20, and 40μ, from 400 mμ upward. The effect here, as well as that for width of spectral band, is more striking for a solution of a neodymium salt or one of the Corning glasses mentioned.

Interesting results are possible with a filter photometer. Use first the three glasses provided with the Fisher instrument; this gives only three points to establish a curve. Then use as many more filters as may be available to fill in intermediate points. Even using six to eight filters leaves much to be desired if one wishes to establish a curve for a substance showing high selectivity in the absorption spectrum.

Conformity of a solution to Bouguer's law. From the curves showing the effect of cell thickness, tabulate the transmittancies for some given wavelength. Preferably, this wavelength should be at a point of minimum transmittancy in the absorption band, which in the case of the permanganate is between 520 and 550 mμ; otherwise a wavelength where the transmittancy differences between different concentrations are large should be selected.

Using the transmittancy for some given cell thickness (such as that for 2 cm) as a basis for calculation, calculate the transmittancy for the other measured thicknesses by means of the relationship

$$T = t^b$$

in which T is the desired transmittancy at thickness b, and t is the transmittancy at unit thickness (in this case, the thickness of the cell used as a basis for calculation). Compare some calculated and measured values for a given thickness.

Conformity of a solution to Beer's law. From the curves in the section on the effect of concentration, tabulate the transmittancies, at the wavelength used in the preceding section, for the several concentrations. Construct a curve with concentration as abscissa and log T as the ordinate, using linear scale paper; or, on semilogarithmic paper, plot T directly

as the ordinate scale (semilog) and concentration as the abscissa on a linear scale. A straight line through the points shows conformity to Beer's law. If preferred, the absorbancy, as given directly on some instruments, may be plotted against concentration, using linear scales.

If conformity to Beer's law is found, calculate the absorbancy indexes for the different concentrations, by means of the relationship

$$a = \frac{A}{bc}$$

in which a = absorbancy index, A = absorbancy, b = thickness, and c = concentration. Using one of the measured values for A and a thickness of 1 cm, calculate the absorbancy index a_M, for a molar solution. Since some papers dealing with spectral absorption use values of log a_M as ordinates, it is interesting to calculate such values for some given concentration of permanganate and then plot the curve from 400 to 700 mμ.

The Beer's law curves serve as calibration curves for making quantitative determinations, as suggested in succeeding exercises. In addition to the readings taken at maximum absorption (525 mμ), those for several other wavelengths may well be plotted to show that maximum sensitivity is attained at minimum transmittancy.

Still another form of calibration curve may be constructed. This is the form recommended by Ringbom (see Figure 17.17, page 272), and consists in plotting transmittancy (or absorptancy) as ordinate, on a linear scale, and concentration, as abscissa, on a logarithmic scale.

Exercise 29.4. Determination of Iron in Water[5]

Iron is one of the elements for which a considerable number of colored forms may be prepared for measurement.[6] Examples of such systems are the complexes formed with concentrated hydrochloric acid, with thiocyanate, and with 1,10-phenanthroline.

Such color-forming reagents are not all equally satisfactory in terms of the general requirements listed in Chapter 17. Thus, none of them is specific. Often the interfering constituents are elements frequently found in practical work.

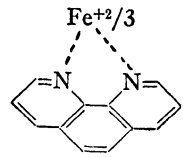
Of a dozen or so possible reagents, 1,10-phenanthroline was selected for this exercise. Since 1930 such cyclic nitrogen compounds have been increasingly used as color-forming reagents. They are colorless, soluble in water, relatively insensitive to *p*H changes between 5 and 9, stable,

[5] See Am. Public Health Assoc., *Standard Methods for the Examination of Water and Sewage*, p. 124 (1955).

[6] See Yoe and Sarver, *Organic Analytical Reagents*, Wiley, 1951.

sensitive, and reasonably free of interference. In contrast to various other reagents, such as thiocyanate, they react with ferrous ion.

1,10-Phenanthroline forms a co-ordinated complex with the iron. The formula for this chelate-type complex is



Apparatus

In this exercise the filter photometer (Fisher Electrophotometer) described in Chapter 17 is specified. Any other comparable visual or photoelectric instrument may be substituted. Since the operating instructions vary with different instruments, those followed should apply to the type of instrument used.

The Fisher instrument is regularly furnished with three relatively nonselective filters, as shown by the transmittance curves in Figures 17.12 and 17.13 (pages 266 and 267). Additional filters are obtainable, of course, and interference filters will greatly increase the selectivity.

The Sample

Selection. Procure enough of the sample to represent the water source to be tested (*1*).

Measurement. With a pipet, transfer 50 ml of the water to a 125-ml conical flask.

Treatment. Add 1 ml of hydrochloric acid (1:9), boil gently to insure dissolution of all iron, and cool the solution to room temperature. Add 1 ml of 10 per cent solution of hydroxylamine (*2*), 10 ml of a 0.10 per cent solution of 1,10-phenanthroline (*3*), and 0.5 ml of concentrated ammonium hydroxide (*4*). Transfer the solution to a 100-ml volumetric flask, dilute to volume with iron-free water, and mix.

The Desired Constituent

Calibration curve. By means of a pipet, transfer 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of a standard solution (*5*) containing 0.1 mg of iron per ml to 100-ml volumetric flasks (*6*). Add to each flask 1 ml of 10 per cent solution of hydroxylamine; then add 2 ml of 0.10 per cent solution of 1,10-phenanthroline for each ml of standard iron solution used. Dilute

the solutions to volume, mix, and allow to stand 10 min. Check the *p*H of the solutions (*4*).

Clean the absorption cells of the instrument. Rinse one of them with some of the solution to be measured and then nearly fill the cell with solution. Wipe with a cleaning tissue (*7*) the faces of the cell through which the light beam is to pass. Clean and fill the blank cell in the same way, using a solution containing all the reagents except the standard iron solution (*8*). Determine the transmittancy or absorbancy of the solution, using a green filter (*9*).

From the readings obtained for the different concentrations, plot a calibration curve. Any one of the forms illustrated in Figures 17.16 and 17.17 (pages 271 and 272) will serve.

Measurement. Measure the unknown solution in the manner followed for establishing the calibration curve. Using the reading obtained, determine from the calibration curve the value for the amount of iron in the unknown solution. Calculate the concentration of the sample in milligrams per liter.

NOTES: (1) Sewage effluents may need special treatment to destroy organic matter and/or to eliminate interfering constituents.[7]

(2) Dissolve 10 g of $NH_2OH \cdot HCl$ in 90 ml of water.

(3) Dissolve 0.10 g of $C_{12}H_8N_2 \cdot H_2O$ in 100 ml of water.

(4) In case of very acidic or basic waters it may be necessary to determine whether the resulting *p*H comes in the range of 5 to 9. For any *p*H that is much beyond these limits, the colored complex is unsatisfactory. The solution should give a pink hue to congo red paper.

(5) Prepare a standard solution containing 0.1 mg of Fe per ml by dissolving 0.7022 g of analytical grade $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\ H_2O$ in 50 ml of distilled water. Transfer to a liter flask, add 1 ml of concentrated sulfuric acid, dilute to volume, and mix.

(6) These volumes are suitable for absorption cells 1 or 2 cm thick and for samples containing 0 to 0.006 mg of iron per ml. Use of more standard solution or thicker absorption cells may be necessary for other conditions.

(7) Such cells must not be scratched.

(8) The blank cell is used to obtain the zero setting in one-cell instruments. In two-cell instruments, the blank solution is placed in the comparison beam.

(9) The preferable wavelength for reading is 508 mμ. A spectrophotometer may be used, of course.

Exercise 29.5. Determination of Nitrite in Water

In the sanitary analysis of water and sewage effluents the nitrite ion is commonly determined colorimetrically.[8] The concentration of this

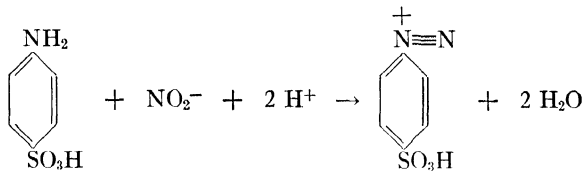
[7] See Butts, Gahler, and Mellon, *Sewage and Ind. Wastes* **22**, 1543 (1950).

[8] See Am. Public Health Assoc., *op. cit.*, p. 153 (1955).

constituent is important primarily in judging the efficacy of purification processes.

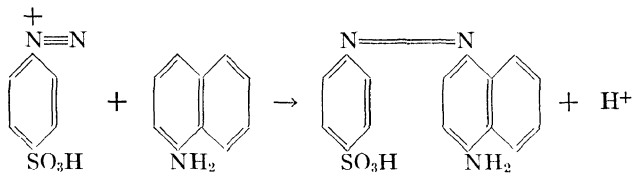
Since an aqueous solution of the nitrite ion itself is colorless, a color has to be developed. The commonly used process takes place in two stages. The interesting chemistry involved in the first stage is the diazotization reaction, so familiar to every organic chemist.

The first step is to allow the nitrite to diazotize 4-aminobenzenesulfonic acid, the first reactant added. The reaction may be represented by the equation



Since hydrogen ion is a reactant, suitable *p*H control must be provided.

Next the diazotate is coupled with 1-napthylamine, according to the equation



Since hydrogen ion is a product in this case, further provision must be made to control this factor in order to obtain a reasonable degree of completion of this reaction.

Incidentally, the process involved in the coupling step indicates the extensive possibilities for obtaining colored systems for measuring organic compounds.

Apparatus

Measurement may be made with a filter photometer using a green filter, such as Corning glass No. 401, or with a spectrophotometer set for 520 mμ.

The Sample

Selection. Procure a sample of adequate size of the water to be tested. Filter, if it is not clear. If the sample is colored, decolorize with aluminum hydroxide (*1*).

Measurement. With a pipet, transfer 50 ml of the sample to a 100-ml volumetric flask. Not over 0.01 mg of nitrite nitrogen should be present (*2*).

The Desired Constituent

Calibration curve. With a suitable measuring pipet, transfer 2.0, 4.0, 6.0, 8.0, 10.0, 15.0, 20.0, and 30.0 ml of the standard nitrite solution (*3*) to 100-ml volumetric flasks. Dilute to approximately 50 ml. Add to each flask 1 ml of a saturated solution of 4-aminobenzenesulfonic acid (*4*). After 5 min. add to each flask 1 ml of 1-naphthylamine solution (*5*) and 1 ml of filtered 2 *M* solution of sodium acetate (*6*). Dilute the solution to volume and mix.

Clean the absorption cells of the photometer. Rinse one of them with some of the solution to be measured and then nearly fill the cell with solution. Wipe with a cleaning tissue (*7*) the faces of the cell through which the light beam will pass. Clean and fill the blank cell in the same way, using a solution containing all the reagents except the standard nitrite solution (*8*). Determine the transmittancy or absorbancy of the solution, using a green filter (*9*).

From the values obtained for the standard solutions plot a calibration curve. Any one of the forms illustrated in Figures 17.16 and 17.17 (pages 271 and 272) will serve.

Measurement. Prepare and measure the unknown solution in the manner followed in preparing the different solutions used for the calibration curve. Using the reading obtained, determine from the calibration curve the value for the amount of nitrite-nitrogen in the unknown sample. Calculate the results in milligrams of nitrite-nitrogen per liter of sample (*2*).

NOTES: (1) See pages 70 and 72 of *Standard Methods for the Examination of Water and Sewage* for the method of discolorization.

(2) Water analysts generally report in terms of nitrogen rather than nitrite.

(3) Prepare a standard nitrite solution by dissolving 0.247 g of analytical-grade sodium nitrite ($NaNO_2$) in 1 liter of water known to be nitrite-free. On dilution of 10 ml of this solution to 1 liter, the resulting solution contains 0.0005 mg of nitrogen per ml.

(4) Dissolve 8 g of 4-aminobenzenesulfonic (sulfanilic) acid in 1 liter of 5 *M* acetic acid.

(5) Dissolve 5 g of 1-naphthylamine in one liter of 5 *M* acetic acid. Filter the solution if not clear.

(6) Dissolve 136 g of sodium acetate, $NaC_2H_3O_2 \cdot 3\ H_2O$, in about 200 ml of water, and dilute to 500 ml.

(7) The absorption cells must not be scratched.

(8) The blank cell is used to obtain the zero setting in one-cell instruments. In two-cell instruments the blank solution is placed in the "blank," or comparison, beam.

(9) The preferable wavelength for reading is 520 mμ. A spectrophotometer may be used.

Exercise 29.6. Determination of Phosphorus Using Heteropoly Compounds

Phosphorus is usually determined colorimetrically by means of transformations involving the orthophosphate ion PO_4^{-3}, which is itself colorless.

In order to obtain a colored measuring form, the analyst may take advantage of a very interesting type of inorganic reaction.[9] In acidic

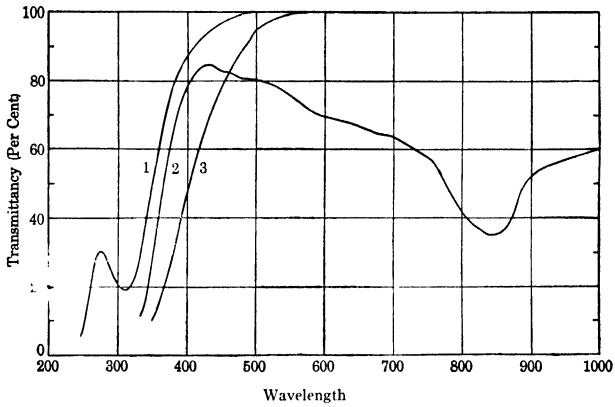


Figure 29.2

Spectral transmission curves of (1) molybdophosphoric acid, (2) reduced molybdophosphoric acid, and (3) molybdovanadophosphoric acid.

solution the phosphoric acid complexes with molybdic acid, H_2MoO_4, to form molybdophosphoric acid. One interpretation of this reaction assumes the substitution of the four oxygens in the phosphate ion PO_4^{-3} by termolybdate[10] ions $Mo_3O_{10}^{-2}$. According to X-ray evidence obtained on a solid product, the formula of the complex is $H_3[P(Mo_3O_{10})_4]$.[11] It is assumed here that this formula applies also in solution. Some writers use the formula $H_3[P(Mo_{12}O_{40})]$.

An aqueous solution of this heteropoly acid has a yellow hue which may be used as the basis for a colorimetric measurement.[12]

[9] Mellon, *Record Chem. Progress* 11, 177 (1950).

[10] The sequence $CrO_4^{-2}\rightarrow$ dichromate $Cr_2O_7^{-2}\rightarrow$ terchromate $Cr_3O_{10}^{-2}$ is known as an equilibrium for isopoly acids.

[11] Sidgwick, *The Chemical Elements and Their Compounds*, p. 1042, Oxford, 1950.

[12] Boltz and Mellon, *Anal. Chem.* 20, 749 (1948).

In the presence of vanadic acid HVO_3, the yellow simple heteropoly acid is transformed to a mixed acid having a deeper hue (somewhat orange). Some analysts give the formula $H_3[P(Mo_{10}V_2O_{39})]$[13] for this complex. Evidently part of the molybdenum in a simple acid is replaced by vanadium. The method included here is for the determination of phosphorus, but an analogous complex, $H_3[P(W_{10}V_2O_{39})]$, may serve for the determination of vanadium.

Finally, either the simple or the mixed acid can be reduced by a variety of substances to a deep-blue solution, of uncertain composition, known as a heteropoly blue. The process may be adapted to the determination of the phosphorus, or some reductant which produces the blue solution.

Figure 29.2 shows the spectrophotometric curves for the simple, mixed, and reduced forms of molybdophosphoric acids. The curves are not for the same concentrations of phosphorus. Inspection of the curves shows that these systems do not possess, in the visual region, absorption bands such as those shown in Figure 17.12 (page 266) for permanganate.

The desirability of taking spectrophotometric curves at or near the peaks of such bands was discussed in Chapter 17. A spectrophotometer having the versatility of the Beckman quartz instrument enables the analyst to take the readings in the near-ultraviolet or infrared, as well as the visual region, of the spectrum. Such adaptability may enable him to move to the region of preferable wavelength.

Apparatus

In order to provide the student with practice in using a spectrophotometer, it is suggested that, if available, such an instrument be used with the procedures outlined below. Simpler apparatus can be used, of course, even visual comparimeters being applicable in the visual region.

Either the Beckman Model DU (quartz optics) or Model B (glass optics) spectrophotometer is recommended. The former enables one to measure well down toward 200 mμ (if the reagents themselves do not absorb in this region). The very expensive quartz absorption cells should be handled with special care.

Method I. Determination of Phosphorus as Molybdophosphoric Acid

The procedure for determining phosphorus as molybdophosphoric acid, $H_3[P(Mo_3O_{10})_4]$, illustrates the use of a simple heteropoly compound for a colorimetric determination. Analogous methods serve for silicon

[13] Ivanov-Emin, *Zhur. Obshcheĭ Khim.* **10**, 826 (1940).

and germanium, using, respectively, molybdosilicic acid, $H_4[Si(Mo_3O_{10})_4]$, and molybdogermanic acid, $H_4[Ge(Mo_3O_{10})_4]$.

The simple acid is less intensely colored (and consequently the method less sensitive) than either the blue reduction product, used in Method II, or the mixed acid, used in Method III.

The general form of the absorption curve for molybdophosphoric acid (Figure 29.2), with no absorption maximum in the visible region, is characteristic of many such yellow solutions. If the spectrophotometer available is limited to the visible region, the analyst must obviously measure on a rather steep portion of the curve, a disadvantage mentioned in Chapter 17. Since this particular system does have a minimum at 310 mμ, he may make the measurement at this wavelength with an instrument such as the Beckman Model DU spectrophotometer, provided the acid is extracted into an organic solvent that transmits at this wavelength.

Several ions interfere seriously with this system; the following, especially, may be mentioned: AsO_4^{-3}, Bi^{+3}, Fe^{+3}, SiO_3^{-2}, WO_4^{-2}, VO_3^{-}. Obviously, these ions must not be present, or provision must be made to eliminate or compensate for the interference.

The Sample

Selection. Select a sample to represent the material to be analyzed (*1*).

Measurement. Measure an amount of sample such that there will be no more than 0.003 mg of phosphorus per 1 ml of sample solution. Transfer to a 50-ml volumetric flask.

Treatment. If the material is a solid, dissolve it in a suitable solvent, but do not use more than 30 to 35 ml. Make the solution neutral to litmus, add 5 ml of 2.8 *M* nitric acid (*2*), and then 5 ml of 10 per cent molybdate solution (*3*). Dilute the solution to volume and mix (*4*).

The Desired Constituent

Calibration curve. With a pipet, transfer portions of 1.0, 2.0, 4.0, 7.0, 10.0, 15.0, 20.0, and 30.0 ml of the standard solution (1 ml = 0.02 mg P) to 50-ml volumetric flasks. Develop a yellow color in the solutions in the same manner as that specified for the preliminary treatment of the unknown solution.

Clean the absorption cells and rinse them with a portion of the solution to be used. With cleaning tissue wipe the outside faces through which the light beam will pass. Transfer to one cell a suitable portion of the

blank solution to be used to set the zero of the instrument. Transfer to another cell a similar portion of one of the known solutions.

Measure the transmittancy or absorbancy of the known solution (*5*). Repeat this measurement for each of the other known solutions. Plot a curve co-ordinating the instrument reading (as ordinate) with concentration (as abscissa). Usable curve forms are shown in Figures 17.16 and 17.17 (pages 271 and 272).

Measurement. For the unknown solutions, follow the same procedure as for the series of knowns.

Using the value obtained, read from the calibration curve the concentration of phosphorus in the sample. Calculate the results in terms of milligrams per liter.

NOTES: (1) As unknowns for this exercise, instructors may find convenient the use of solid samples prepared by mixing well in a ball mill 100-mesh potassium nitrate with minute amounts of 100-mesh potassium dihydrogen phosphate. Because of the low percentage range of phosphorus that will be used, the use of dilute solutions of the phosphate may be considered preferable.

To prepare a stock solution, dissolve 4.387 g of dried potassium dihydrogen phosphate, KH_2PO_4, in a 500-ml flask, make just acidic with HNO_3, and dilute to volume. Each milliliter contains 0.12 mg of phosphorus. Such a solution may slowly dissolve silica out of a glass container; if so, an error will occur, since molybdosilicic acid is yellow in solution.

(2) This amount of acid is approximately optimum for maximum color development.

(3) Transfer 50 g of sodium molybdate $Na_2MoO_4 \cdot 2\ H_2O$, to a 500-ml volumetric flask, dissolve in water, and dilute to volume.

(4) The color develops quickly and is stable for at least 1 hour.

(5) If the spectrophotometer operates in the ultraviolet, take the readings at 380 mμ; otherwise, use 400 or 420 mμ.

Method II. Determination of Phosphate Phosphorus in Water as Molybdenum Blue[14]

Solutions of heteropoly acids are easily reduced by a variety of substances to give blue solutions, known as heteropoly blues. If molybdenum is the co-ordinated metal in the complex, the solution is commonly known as molybdenum blue. There is yet no agreement regarding the nature of the reduced product.

For two solutions containing the same amount of phosphorus, one as yellow molybdophosphoric acid and the other as molybdenum blue, the latter is much more intensely colored. Consequently, this method is the more sensitive of the two.

Since many reductants produce the blue system, there is a choice of

[14] Adapted from Am. Public Health Assn., *op. cit.*, p. 79 (1946).

reagents. Some analysts prefer organic, some inorganic substances. Well-known reagents are chlorostannous acid, hydroquinone, 1-amino-2-naphthol-4-sulfonic acid, benzidine, a reduced molybdate, hydroxylamine, hydrazine sulfate, sodium sulfite, and others. The reductant selected for this exercise is 1-amino-2-naphthol-4-sulfonic acid, $NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H$.

The Sample

Selection. Procure an adequate portion of the sample to be tested. Filter, if it is not clear.

Measurement. With a pipet, transfer 50 ml of the water to a 100-ml volumetric flask.

Add a drop of phenolphthalein indicator. If there is a pink hue, add sufficient H_2SO_4 (1:3) to discharge the color. Then add 1 ml excess of this acid.

Dilute the solution to about 70 ml with water. Add 10 ml of molybdate solution (*1*) and mix. Then add 4 ml of sulfonic acid reductant (*2*). Dilute to 100 ml and mix well. Allow 5 min. for color development.

The Desired Constituent

Calibration curve. With a pipet, transfer portions of 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, and 10.0 ml of the standard phosphate solution (1 ml = 0.05 mg PO_4) to 100-ml volumetric flasks (*3*). Develop a blue hue in the solutions in the same manner as that specified for the preliminary treatment of the unknown solution.

Clean the absorption cells and rinse them with a portion of the solution to be measured. With cleaning tissue wipe the outside faces of the cells through which the light beam will pass. Transfer to one cell a suitable portion of the blank solution to be used to set the zero of the instrument (*4*). Transfer to another cell a similar portion of one of the known solutions.

Measure the transmittancy or absorbancy of the known solution (*5*). Repeat this measurement with each of the other known solutions. Plot a curve co-ordinating the instrument reading (as ordinate, with concentration (as abscissa). Usable curve forms are shown in Figures 17.16 and 17.17 (pages 271 and 272).

Measurement. With the unknown samples, follow the same procedure as for the series of knowns.

Using the value obtained, read from the calibration curve the concen-

tration of phosphate in the sample. Calculate the results in terms of milligrams per liter according to the expression

$$\text{Mg/liter} = (\text{mg}/50\ \text{ml}) \times 20$$

NOTES: (1) Dissolve 25 g of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$, in 200 ml of distilled water. Add 500 ml of sulfuric acid (1:3) and dilute to 1 liter with water.

(2) Grind 0.5 g of analytical-grade 1-amino-2-naphthol-4-sulfonic acid, $NH_2 \cdot C_{10}H_5(OH) \cdot SO_3H$, take up with 5 ml of sodium sulfite solution (20 g Na_2SO_3 per 100 ml), and dissolve in 195 ml of sodium pyrosulfite solution (150 g $Na_2S_2O_5$ per liter). Too much sodium sulfite decreases the stability of the reagent. Heat the solution, if necessary, to 50 to 60° to hasten dissolution. Keep the solution in a dark bottle, and prepare fresh every 2 weeks.

(3) Dissolve 7.164 g of dried potassium dihydrogen phosphate, KH_2PO_4, in 1 liter of distilled water. Dilute 10 ml of this solution to 1 liter. Each milliliter then contains 0.05 mg PO_4.

(4) If the unknown water is colored, use some of it as a blank. Otherwise, water alone may be used.

(5) If the spectrophotometer operates in the near-infrared region, take the readings at 820 mμ. Use 650 mμ for instruments operating only in the visual region.

Method III. Determination of Phosphorus in Copper-Base Alloys as Molybdovanadophosphoric Acid[15]

This colorimetric method, as given, is recommended for alloys containing 0.01 to 0.2 per cent of phosphorus, with or without tin. It may be adapted for higher ranges of phosphorus. Although arsenic and silicon form simple heteropoly compounds, they do not interfere in this method in amounts less than 1 per cent.

The use of phosphorus-free copper as a blank illustrates one kind of compensation of error. The color of the cupric ion in the blank balances that of the cupric ion in the unknown.

The Sample

Selection. Procure fine drillings or millings representative of the alloy to be analyzed.

Measurement. Weigh amounts of 1.000 g of the sample, and of a low-phosphorus copper blank (*1*), and transfer to 150-ml beakers.

For preparation of the calibration curve, weigh 1.000-g portions of low-phosphorus copper and transfer to each of ten 150-ml beakers. Pipet portions of 2.0, 4.0, 6.0, 8.0, and 10.0 ml of phosphorus solution *A* (*2*) to five of the beakers, and portions of 4.0, 6.0, 8.0, and 10.0 ml

[15] Adapted from Am. Soc. Testing Materials, *1950 Book of ASTM Methods for Chemical Analysis of Metals*, p. 294.

of phosphorus solution *B* (*3*) to four of the beakers. Reserve the tenth beaker for a blank.

Treatment. To each of the beakers, containing unknown, blanks, and knowns, add 15 ml of mixed acids (*4*) and a few grains of silicon carbide (*5*). Cover with glasses and heat moderately until dissolution is complete.

Add 1 ml of hydrogen peroxide (*6*) to each solution, and boil gently for 3 to 5 min. (*7*). Remove from the heat, add 5 ml of ammonium vanadate solution (*8*), cool to room temperature, and transfer to a 50-ml volumetric flask. Add 5 ml of ammonium molybdate solution (*9*), dilute to volume, and mix. Allow 5 min. for development of the color (*10*).

The Desired Constituent

Calibration curve. Clean the absorption cells and rinse them with a portion of the solution to be measured. With cleaning tissue wipe the outside faces through which the light beam will pass. Transfer a suitable portion of the blank solution to the cell to be used to set the "zero" of the instrument (*11*). In another cell, place a similar portion of one of the knowns. Measure the transmittancy or absorbancy of the solution at 470 mμ. Repeat this measurement for each of the known solutions.

Plot a calibration curve, co-ordinating instrument reading (as ordinates) with milligrams of phosphorus per 50 ml (as abscissa). See Figures 17.16 and 17.17 (pages 271 and 272) for commonly used forms of curves.

Measurement. For the unknown samples follow the same procedure as for the known samples.

Using the values obtained, read the milligrams of phosphorus in the sample. The percentage of phosphorus is obtained by the usual calculation

$$\text{Phosphorus, per cent} = \frac{\text{mg of P}}{\text{g of sample} \times 10}$$

NOTES: (1) Use copper containing less than 0.0002 per cent phosphorous.

(2) Solution *A*. Dissolve 0.9156 g of disodium hydrogen phosphate, Na_2HPO_4, in about 200 ml of water. Add 50 ml of nitric acid (1:5) and dilute to 1 liter in a volumetric flask. Each milliliter = 0.2 mg of P.

(3) Solution *B*. Dilute 1 volume of Solution *A* (1 ml = 0.2 mg P) with 3 volumes of water. Each milliliter = 0.05 mg P.

(4) Add 320 ml of nitric acid and 120 ml of hydrochloric acid to 500 ml of water. Cool and dilute to 1 liter.

(5) The particles help to prevent bumping.

(6) Dilute 10 ml of 30 per cent hydrogen peroxide to 100 ml. Store the solution in a dark bottle in a cool place.

(7) Avoid prolonged boiling, since excessive loss of acid will affect subsequent development of color. Heteropoly colors develop best within certain *p*H limits.

(8) Dissolve 2.50 g of ammonium vanadate, NH_4VO_3, in 500 ml of hot water. Add 20 ml of nitric acid (1:1), cool, and dilute to 1 liter.

(9) Dissolve 100 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$, in 600 ml of water at 50°C and dilute to 1 liter. Filter before use.

(10) The color is stable for at least 1 hr.

(11) With single-beam instruments, such as the Beckman Models DU and B, the blank cell is inserted and the instrument adjusted until the needle reads 100 on the "Transmittance" scale of zero on the "Absorbance" scale. The blank is then replaced with an unknown (or one of the knowns) for its reading.

With double-beam instruments, such as the General Electric, the blank cell is placed in the "blank" beam and the unknown (or one of the knowns) in the other beam. The subsequent reading is then a direct measure of the transmittancy or absorbancy of the sample.

Exercise 29.7. ASTM Tentative Photometric Methods for Chemical Analysis of Magnesium and Magnesium-Base Alloys[16]

ASTM Designation: E 35-50 T
Issued, 1946; Revised, 1950

These Tentative Methods have been approved by the sponsoring committee and accepted by the Society in accordance with established procedures, for use pending adoption as standard.

Scope

1. (*a*) These methods cover photometric procedures[17] for the chemical analysis of magnesium and magnesium-base alloys having chemical compositions within the following limits:

Aluminum	0.0 to 12
Zinc	0.0 to 5
Manganese	0.0 to 2
Calcium	0.0 to 1.0
Lead	0.001 to 0.5
Silicon	0.005 to 0.05[18]

[16] This is an all-absorptimetric method of analysis for magnesium and magnesium-base alloys. As is typical of such industrial methods, the major constituent, magnesium, if reported at all, is taken by difference.

The material in this section is reproduced, with minor changes, with permission of the American Society for Testing Materials.

The methods are given, insofar as is feasible, in their original form, in order that students may gain experience in dealing with widely used industrial methods. [*Author*]

[17] These procedures, unless otherwise indicated, have been written for a cell having a 1-cm light path. Cells having other dimensions may be used, provided suitable adjustments can be made in the amounts of sample and reagents used.

[18] Alloys of higher silicon content (up to 0.8 per cent silicon) may generally be analyzed for elements other than silicon by these methods.

Copper	0.005 to 0.05
Iron	0.002 to 0.05
Nickel	0.0 to 0.05
Magnesium	remainder

Photometric Practice, Apparatus, and Reagents

2. (*a*) *Photometers and Photometric Practice.* Photometers and photometric practice prescribed in these methods shall conform to the Tentative Recommended Practice for Photometric Methods for Chemical Analysis of Metals (ASTM Designation: E 60).[19]

(*b*) Apparatus other than photometers, standard solutions, and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in the Recommended Practices for Apparatus and Reagents for Chemical Analysis of Metals (ASTM Designation: E 50).[20]

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Manganese by the Periodate Method

Principle of Method

6. Manganese in an acidic solution is oxidized to permanganate by means of potassium periodate. Photometric measurement is made at approximately 550 mμ.

Concentration Range

7. The recommended concentration range is from 0.2 to 2.5 mg of manganese in 100 ml of solution, using a cell depth of 1 cm.

Stability of Color

8. The permanganate color is stable indefinitely if reducing substances are absent.

Interfering Elements

9. The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in Section 1 (*a*). At least ten times as much cerium as manganese may be present without causing interference.

[19] Am. Soc. Testing Materials, *1950 Book of ASTM Methods for Chemical Analysis of Metals*, p. 43.

[20] Am. Soc. Testing Materials, *1950 Book of ASTM Methods for Chemical Analysis of Metals*, p. 1.

Reagents

10. *Standard Manganese Solution (1 ml = 0.10 mg Mn).* Dissolve 0.100 g of high-purity manganese in 10 ml of HNO_3 (1:1) and boil to expel brown fumes. Cool, dilute to 1 liter in a volumetric flask, and mix. Alternatively, the solution may be prepared as follows: Dissolve 2.88 g of $KMnO_4$ in about 200 ml of water, add 20 ml of H_2SO_4 (1:1), and reduce the permanganate solution by additions of Na_2SO_3 or H_2O_2. Boil to remove excess SO_2 or H_2O_2, cool, dilute to 1 liter in a volumetric flask, and mix. Dilute 100 ml of this solution to 1 liter in a volumetric flask and mix.

Preparation of Calibration Curve

11. (*a*) Transfer 5.0, 10.0, and 20.0-ml aliquots of manganese solution (1 ml = 0.10 mg Mn) to 250-ml beakers. To each beaker, and to an additional beaker to be carried through as a blank, add 15 ml of H_2SO_4 (1:4) and 25 ml of HNO_3 that has been freshly boiled to expel lower oxides of nitrogen.

(*b*) To each beaker, add 5 ml of H_3PO_4 and a few granules of silicon carbide, heat almost to boiling, and carefully introduce 0.5 g of KIO_4. Boil for 3 min. and then digest just below the boiling point for 15 min. to develop the full intensity of color. Cool, dilute to 100 ml in a volumetric flask, and mix.

(*c*) Transfer a suitable portion of the solution to an absorption cell and measure the transmittancy or absorbancy at approximately 550 mμ. Compensate or correct for the blank.

(*d*) Plot the values obtained against milligrams of manganese per 100 ml of solution.

Procedure

12. (*a*) For alloys of low-manganese content (under 0.5 per cent) transfer a weighed portion of the sample, preferably containing from 0.5 to 2.0 mg of manganese, to a 250-ml beaker. Carry through a blank on the reagents. Add 25 ml of water and dissolve in H_2SO_4 (1:4), using approximately 25 ml of H_2SO_4 (1:4) per gram of sample. When the action ceases, add 25 ml of HNO_3 and heat to dissolve any dark residue. If the solution is turbid, filter. Continue in accordance with Section 11 (*b*) and (*c*).

(*b*) For alloys of high manganese content (0.5 per cent and over) transfer a weighed portion of the sample, preferably containing from 10 to 15 mg of manganese, to a 250-ml beaker. Carry through a blank

on the reagents. Add 25 ml of water, and dissolve in H_2SO_4 (1:4), using approximately 25 ml of H_2SO_4 (1:4) per gram of sample. When the action ceases, add 5 ml of HNO_3 and heat to dissolve any dark residue. If the solution is turbid, filter. Dilute the solution to 250 ml in a volumetric flask and transfer a 25-ml aliquot to a 25-ml beaker. Add 15 ml of H_2SO_4 (1:4) and 25 ml of HNO_3. Continue in accordance with Section 11 (*b*) and (*c*).

(*c*) Using the value obtained, read from the calibration curve the number of milligrams of manganese present in 100 ml of the final solution.

(*d*) *Calculation.* Calculate the percentage of manganese as follows:

$$\text{Manganese, per cent} = \frac{A}{B \times 10}$$

where,

A = milligrams of manganese found in 100 ml of the final solution and
B = grams of sample represented in 100 ml of the final solution.

Copper by the Hydrobromic Acid–Phosphoric Acid Method

Scope

13. This method covers a procedure for the determination of 0.005 to 0.06 per cent of copper in magnesium metal, magnesium-base alloys, and scrap for remelting.

Principle of Method

14. Cupric copper forms a violet-colored complex in strong HBr solution. Phosphoric acid is added to minimize interference from iron and the photometric measurement is made at approximately 600 mμ.

Concentration Range

15. The recommended concentration range is from 0.05 to 1.5 mg of copper per 25 ml of solution, using a cell depth of 1 cm.

Stability of Color

16. The color is stable for at least 2 hr.

Interfering Elements

17. The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in Section 1 (*a*). Molybdenum, vanadium, chromium, cobalt, gold, the platinum metals, and certain elements of the rare-earth group would cause interference if present. Iron or nickel may cause somewhat high results

if present in an amount equalling or exceeding the amount of copper. Provision is made in the method for separation of copper from all elements but the noble metals.

Reagents

18. (*a*) *Standard Copper Solution* (*1 ml = 0.02 mg Cu*). Dissolve 0.2000 g of copper in 15 ml of HBr containing 1 ml of bromine and dilute to 250 ml in a volumetric flask. Dilute 25 ml of this solution to 1 liter in a volumetric flask and mix.

(*b*) *Hydrobromic Acid–Bromine Solution.* Add one drop of bromine to 250 ml of HBr and mix.

(*c*) *Bromine Water* (*saturated*).

Preparation of Calibration Curve

19. (*a*) Transfer 5.0, 10.0, and 25.0 ml of copper solution (1 ml = 0.02 mg Cu) to three 100-ml beakers. To each beaker, and to an additional beaker to be carried through as a blank, add 3 ml of HBr-Br_2 solution and a few drops of bromine water. Evaporate to 3 ml, or slightly less, and cool. Add 3 ml of HBr-Br_2 solution plus 12.5 ml of H_3PO_4 and pour into a 25-ml glass-stoppered volumetric flask. Rinse the beaker with small portions of HBr-Br_2 solution and transfer these also to the flask. Dilute to the mark with HBr-Br_2 solution and mix well.

(*b*) Transfer a suitable portion of the solution to an absorption cell. If the photometer has an exposed photocell, the photocell may be protected from HBr vapors by inserting next to it a water-filled absorption cell. Measure the transmittancy or absorbancy at 600 mμ and compensate or correct for the blank.

(*c*) Plot the values obtained against milligrams of copper per 25 ml of solution.

Procedure

20. (*a*) Weigh a sample of not more than 1.00 g containing from 0.1 to 1.2 mg of copper, but with no more iron or nickel than copper.[21] Place

[21] To remove iron or nickel, place 0.5 to 1.0 g of the sample in a 250-ml beaker and treat with small portions of HCl (2:3) until a total of 25 ml per gram of sample has been added. After the reaction subsides, add a few drops of H_2O_2 to facilitate [dis]solution of all copper. Boil the solution to remove chlorine, then dilute to about 50 ml and add 1 g of finely granulated, low-copper lead. Bring the solution to a boil and continue gentle boiling for 15 min. to displace the copper completely. Cool and decant the solution, washing once with water. (The solution may be placed in a separatory funnel and used for determination of nickel by the dimethylglyoxime photometric method.) Warm the beaker containing the lead and copper gently to remove moisture; then dissolve the metal in 10 ml of HBr and a few drops of liquid bromine. Boil to expel the bromine and continue in accordance with Section 20 (*b*), beginning with the addition of H_3PO_4.

in a 100-ml beaker and add 25 ml of water. Treat with HBr-Br_2 solution, adding it in small portions and using a total of 10 ml per gram of sample, plus an excess of 3 ml. Warm to dissolve all the metal, adding a little bromine water if necessary. Carry through a blank on the reagents.

(*b*) Cool, transfer to a 50-ml volumetric flask, dilute to the mark and mix. Pipet a 25-ml aliquot into a 100-ml beaker, add enough bromine water to produce a yellow color, and evaporate to 3 ml or slightly less. Add 3 ml of HBr-Br_2 solution plus 12.5 ml of H_3PO_4 and warm to dissolve all soluble salts. Cool and pour the mixture into a 25-ml glass-stoppered volumetric flask. Rinse the beaker with small portions of HBr-Br_2 solution and place these also in the flask. Dilute to the mark with HBr-Br_2 solution. Mix well and filter off any insoluble material on a dry, fritted-glass crucible. Continue as described in Section 19 (*b*). If too much copper is present for satisfactory reading, dilute the solution to a larger volume with equal volumes of HBr-Br_2 solution and H_3PO_4 and take account of the dilution in the calculation, or repeat using a smaller aliquot of the sample. Do not dilute with water, for this causes fading of the color.

(*c*) Using the value obtained, read from the calibration curve the number of milligrams of copper present in 25 ml of solution.

(*d*) *Calculation.* Calculate the percentage of copper as follows:

$$\text{Copper, per cent} = \frac{A}{B \times 10}$$

where,

A = milligrams of copper found in 25 ml of the final solution, and
B = grams of sample represented in 25 ml of the final solution.

Nickel by the Dimethylglyoxime Extraction Method

Scope

21. This method covers a photometric procedure for the determination of 0.0005 to 0.005 per cent of nickel in magnesium metal, magnesium-base alloys, and scrap for remelting.

Principle of Method

22. Nickel is separated from other metals by reaction with dimethylglyoxime and extraction with chloroform. After further extraction with acid, nickelic dimethylglyoxime is formed through oxidation with bromine and is determined photometrically at approximately 530 mμ.

Concentration Range

23. The recommended concentration range is from 0.005 to 0.050 mg of nickel in 100 ml of solution, using a cell depth of 5 cm.

Stability of Color

24. The color intensity increases slowly on standing. Readings should be made about 10 min. after mixing.

Interfering Elements

25. Under the conditions specified, no interference is encountered from the elements normally present in magnesium-base alloys.

Reagents

26. (*a*) *Standard Nickel Solution* (*1 ml = 0.005 mg Ni*). Dissolve 0.1000 g of nickel by warming with successive small portions of HCl, diluting with water, and pouring off into a 1-liter volumetric flask. When all the nickel is dissolved, bring to room temperature and dilute to 1 liter. Dilute 25 ml of this solution to 500 ml in a volumetric flask and mix. Optionally, the original solution may be prepared from a nickel salt and standardized gravimetrically.

(*b*) *Sodium Citrate Solution* (*88 g per l*). Dissolve 100 g of sodium citrate dihydrate in water, dilute to 1 liter, and mix.

(*c*) *Alcohol Solution of Dimethylglyoxime* (*10 g per l*). Reagent No. 104.

(*d*) *Bromine Water* (*saturated*).

(*e*) *Hydroxylamine Hydrochloride Solution* (*50 g $NH_2OH \cdot HCl$ per l*). Dissolve 5 g of $NH_2OH \cdot HCl$ in water and dilute to 100 ml. This solution shall be freshly prepared.

Preparation of Calibration Curve

27. (*a*) Pipet 1.0, 2.0, 5.0, 7.0, and 10.0 ml of nickel solution (1 ml = 0.005 mg Ni) into 200-ml separatory funnels containing 50 ml of water. Add 2 ml of HNO_3 and 10 ml of sodium citrate solution to each funnel, and to an additional funnel for use as a blank.

(*b*) Neutralize each solution to litmus by dropwise addition of NH_4OH, adding a few drops in excess. Introduce 3 ml of dimethylglyoxime solution, mix, and allow to stand for at least 5 min. Extract with three 10-ml portions of chloroform and combine the chloroform layers in a clean separatory funnel. Wash the combined extracts with a 25-ml portion of NH_4OH (2:98) and draw off the chloroform into another clean separatory funnel. Extract the ammoniacal layer with two 2-ml

portions of chloroform, and add them to the rest. Shake the chloroform for 1 min. each with two portions of HCl (1:19), using 25 ml the first time and 15 ml the second. Draw off the final chloroform layer, separating it as completely as possible, and discard. Draw both acid layers into a 100-ml volumetric flask.

(*c*) To the combined acid extracts add 5 drops of saturated bromine water, followed by NH_4OH (1:1) added dropwise until the bromine color is destroyed and then an excess of 3 or 4 drops. Add 0.5 ml of dimethylglyoxime solution, dilute to 100 ml with water, and mix.

(*d*) Transfer a suitable portion of the solution to an absorption cell and, 10 min. after adding the dimethylglyoxime solution, measure the transmittancy or absorbancy at a wave length of approximately 530 mμ. Compensate or correct for the blank.

(*e*) Plot the values obtained against milligrams of nickel per 100 ml of final solution.

Procedure

28. (*a*) Transfer from 1.00 to 1.50 g of the sample to a 250-ml beaker. Add 40 ml of water, and dissolve by gradually adding 10 ml of HCl and 2 ml of HNO_3. Prepare a blank also with water and the acids. Cool and transfer to a 200-ml separatory funnel, using but little water so that the total volume does not exceed 60 ml. Add 10 ml of citrate solution, or more if aluminum is unusually high. If manganese is also present, introduce 5 ml of hydroxylamine hydrochloride solution. Continue as described in Section 27 (*b*) to (*d*).

(*b*) Using the value obtained, read from the calibration curve the number of milligrams of nickel present in 100 ml of final solution.

(*c*) *Calculation.* Calculate the percentage of nickel as follows:

$$\text{Nickel, per cent} = \frac{A}{B \times 10}$$

where,

A = milligrams of nickel found, and
B = grams of sample used.

Iron by the Bipyridine Method

Principle of Method

29. Ferrous iron in a solution having a *p*H of 3 to 4 [22] forms a pink-colored complex with 2,2′-bipyridine. Photometric measurement is made at approximately 520 mμ.

[22] Control of the *p*H between 3 and 4 is necessary, since at lower *p*H values the color fades while at higher values there is danger of precipitating aluminum.

Concentration Range

30. The recommended concentration range is from 0.01 to 0.12 mg of iron in 50 ml of solution, using a cell depth of 5 cm.

Stability of Color

31. The color is stable for several hours, and probably for a much longer period, if the solution is protected against oxidation.

Interfering Elements

32. The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in Section 1 (*a*). Copper over 0.05 per cent may interfere by forming a green complex with bipyridine. Excessive amounts of zinc interfere by forming a colorless complex with bipyridine.

Reagents

33. (*a*) *Standard Iron Solution* (*1 ml = 0.01 mg Fe*). Dissolve 0.0864 g of $FeNH_4(SO_4)_2 \cdot 12\ H_2O$ in 100 ml of HCl (1:19) and dilute to 1 liter in a volumetric flask.

(*b*) *Bipyridine Solution* (*10 g per l*). Dissolve 0.2 g of 2,2′-bipyridine in 2 ml of HCl (1:9) and 18 ml of water. This solution should be prepared not more than three days before use.

(*c*) *Sodium Sulfite Solution* (*100 g Na_2SO_3 per l*). Dissolve 10 g of Na_2SO_3 in 100 ml. of water. This solution should be prepared not more than three days before use.

Preparation of Calibration Curve

34. (*a*) Transfer 2.0, 5.0, 10.0, and 15.0-ml aliquots of iron solution (1 ml = 0.01 mg Fe) to 150-ml beakers. Carry through a blank on the reagents.

(*b*) Evaporate the solutions to dryness on a steam bath. Cool, and completely dissolve the residue in 2.0 ml[22] of HCl (1:9). Add 10 to 15 ml of water, 2.0 ml of bipyridine (10 g per l)[23] and 1 ml of Na_2SO_3 (100 g per l).[24] Stir and allow to stand for 2 min. Add 2 ml of Na_2SO_3 (100 g per l), dilute to 50 ml in a volumetric flask, and mix. If the solution is turbid, filter through a dry filter. When over 0.02 mg of iron is present, a low-ash filter paper may be used, but for smaller amounts a fritted-glass filtering crucible is preferable.

[23] The quantity of bipyridine specified is sufficient to complex up to 0.012 g of zinc and also to produce the colored iron complex.

[24] Sodium sulfite serves both as a reducing agent and as a buffer.

(*c*) Transfer a suitable portion of the solution to an absorption cell having a 5-cm light path and measure the transmittancy or absorbancy at approximately 520 mμ. Compensate or correct for the blank.

(*d*) Plot the values obtained against milligrams of iron per 50 ml of solution.

Procedure

35. (*a*) Transfer a weighed portion of the sample (1 to 3 g), preferably containing from 0.01 to 0.5 mg of iron, and free of adventitious iron, to a 250-ml beaker. Add 50 ml of water and dissolve by slowly adding HCl, using 7 ml per gram of sample used and adding an excess of 5 ml. Carry through a blank on the reagents.

(*b*) When dissolution is complete, boil the solution for a few minutes. If the iron content is under 0.12 mg and the aluminum content is under 20 mg, continue in accordance with Section 34 (*b*) and (*c*). Otherwise continue in accordance with Paragraph (*c*) of this section.

(*c*) Cool, dilute to 100 ml in a volumetric flask, and mix. Transfer an aliquot containing from 0.01 to 0.12 mg of iron, but preferably under 20 mg of aluminum, to a 150-ml beaker and evaporate until the volume is reduced to 2 to 5 ml. Continue in accordance with Section 34 (*b*) and (*c*).

(*d*) Using the value obtained, read from the calibration curve the number of milligrams of iron present in 50 ml of the final solution.

(*e*) *Calculation.* Calculate the percentage of iron as follows:

$$\text{Iron, per cent} = \frac{A}{B \times 10}$$

where,

A = milligrams of iron found in 50 ml of the final solution, and
B = grams of sample represented in 50 ml of the final solution.

Silicon by the Molybdosilicic Acid Method

Principle of Method

36. Silicic acid in a true (not colloidal) solution reacts with molybdate in a sulfuric acid solution, to form a soluble yellow-colored molybdosilicic acid. Photometric measurement is made at approximately 420 mμ.

Concentration Range

37. The recommended concentration range is from 0.03 to 0.4 mg of silicon in 100 ml of solution, using a cell depth of 5 cm.

Stability of Color

38. The color is stable for about 1 hour.

Interfering Elements

39. The elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in Section 1 (*a*). Phosphates cause a yellow color that interferes.[25]

Reagents

40. (*a*) *Standard Silicon Solution* (*1 ml = 0.05 mg Si*). Fuse 0.1070 g of SiO_2 with 1.0 g of Na_2CO_3 in a platinum crucible. Cool the melt, dissolve completely in water and dilute to 1 liter in a volumetric flask. The solution should be kept in a paraffined bottle, or prepared fresh as needed.

(*b*) *Ammonium Molybdate Solution* (*75 g* $(NH_4)_6Mo_7O_{24}$ *per l*). Dissolve 40 g of $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ in 500 ml of water.

(*c*) *Boric Acid Solution* (*saturated*).

(*d*) *Sulfuric Acid* (*1:4*). Prepare fresh as needed.

Preparation of Calibration Curve

41. (*a*) Transfer 2.0, 5.0, and 10.0-ml aliquots of silicon solution (1 ml = 0.05 mg Si) to 100-ml volumetric flasks. To each flask, and to an additional flask for a blank, add 40 ml of water, 1.0 ml of H_2SO_4 (1:4), and 10 g of $MgSO_4 \cdot 7\ H_2O$. When the $MgSO_4$ has dissolved, add 5.0 ml of ammonium molybdate (75 g per 1), dilute to 100 ml, and mix.[26]

(*b*) Transfer a suitable portion of the solution to an absorption cell having a 5-cm light path and measure the transmittancy or absorbancy at approximately 420 mμ. Compensate or correct for the blank.

(*c*) Plot the values obtained against milligrams of silicon per 100 ml of solution.

Procedure

42. (*a*) Transfer a weighed portion of the sample (under 2 g) containing not more than 1 mg of silicon to a 150-ml beaker. Add 25 ml of water and 5 ml of a saturated solution of H_3BO_3. Add, in small quantities, 11.7 ml of H_2SO_4 (1:4) per gram of sample, meanwhile keep-

[25] It appears from the literature that a given weight of phosphorus yields slightly less than half as much color as the same weight of silicon. The possible interferences from elements such as tin, arsenic, or cerium have not been investigated.

[26] The yellow color ordinarily develops within 5 min. and should be read within 1 hr. after addition of molybdate, since fading takes place after a longer time.

ing the beaker in a cold water bath to prevent losses of silicon as hydride. Add 1.0 ml of H_2SO_4 (1:4) in excess. Carry through a blank on all the reagents and the filter paper, except that only 1 ml of H_2SO_4 (1:4) shall be used per 100 ml of solution, since the color is affected by the acidity.

(*b*) When the sample is dissolved, introduce 0.1 g of $K_2S_2O_8$ to oxidize ferrous iron or other reducing agents. Allow to stand for 10 min. or longer, dilute to about 60 ml with water, and filter through a close-texture, low-ash paper, catching the filtrate in a 100-ml volumetric flask. Rinse the beaker and paper with enough water to dilute the filtrate to approximately 90 ml. Reserve the filtrate.

(*c*) Place the filter paper in a clean platinum crucible and ignite at 500°C. Add 0.1 g of Na_2CO_3 and fuse at approximately 850°C. Dissolve the residue in water with enough H_2SO_4 (1:4) to neutralize the Na_2CO_3, plus 1 ml in excess, and filter through a close-texture, low-ash paper into another 100-ml volumetric flask. Rinse the beaker and paper with enough water to dilute the filtrate to approximately 90 ml.

(*d*) To each flask (Paragraphs (*b*) and (*c*)) add 5.0 ml of ammonium molybdate (75 g per l). If a green color develops due to the presence of reducing agents, add 0.1 g of $K_2S_2O_8$. Dilute to 100 ml [27] and mix. Continue in accordance with Section 41 (*b*). Compensate or correct for the appropriate blanks.

(*e*) Using the value obtained, read from the calibration curve the number of milligrams of silicon present in 100 ml of each solution. Add together the amounts found in the original filtrate (Paragraph (*b*)) and in the dissolved residue (Paragraph (*c*)).

(*f*) *Calculation.* Calculate the percentage of silicon as follows:

$$\text{Silicon, per cent} = \frac{A}{B \times 10}$$

where,

A = milligrams of silicon found (Paragraph (*c*)), and
B = grams of sample used.

Lead by the Dithizone Method

Principle of Method

43. Lead reacts with diphenylthiocarbazone to form a pink-colored complex in a chloroform solution. The complex is separated from other metals by extraction of an aqueous, ammonium citrate-cyanide solution

[27] For samples containing over 1 mg of silicon, aliquots may be taken. In every case the final solutions should contain 1.0 ml of H_2SO_4 (1:4) and 5.0 ml of ammonium molybdate (75 g per l) per 100 ml.

with chloroform. Photometric measurement is made at approximately 520 mμ.

Concentration Range

44. The recommended concentration range is from 0.002 to 0.014 mg of lead in 10 ml of solution, using a cell depth of 1 cm.

Stability of Color

45. The color is quite stable if the solution is protected against evaporation and decomposition of the chloroform. Due to the nature of the solvent, it is advisable to make the reading promptly.

Interfering Elements

46. In general, the elements ordinarily present in magnesium alloys do not interfere if their contents are under the maximum limits shown in Section 1 (*a*).[28]

Reagents

47. (*a*) *Standard Lead Solution* (*1 ml = 0.001 mg Pb*). Dissolve 0.1342 g of $PbCl_2$ in water containing 1 ml of HCl and dilute to 1 liter in a volumetric flask. Add 0.5 ml of HCl to 10 ml of this solution and dilute to 1 liter in a volumetric flask. Prepare fresh as required.

(*b*) *Ammonium Citrate Solution* (*50 g per l*). Dissolve 40 g of citric acid in water, neutralize with NH_4OH and dilute to 1 liter.

(*c*) *First Extraction Solution.* To 435 ml of water, add 30 ml of KCN (50 g per l), 30 ml of ammonium citrate (50 g per l), and 5 ml of NH_4OH.

(*d*) *Second Extraction Solution.* To 500 ml of water add 10 ml of KCN (50 g per l) and 5 ml of NH_4OH.

(*e*) *Dithizone Solution.* Dissolve 0.0025 g of diphenylthiocarbazone in 100 ml of chloroform.

(*f*) *Chloroform.*

Preparation of Calibration Curve

48. (*a*) Transfer 2.0, 5.0, 10.0, and 15.0-ml aliquots of lead solution (1 ml = 0.001 mg Pb) to separatory funnels[29] of approximately 100-ml

[28] Bismuth, thallium, indium, and stannous tin interfere but are not likely to be present in magnesium alloys. Bismuth can be determined and compensated for through the use of suitable calibration curves if another reading is made at 420 to 450 mμ. Tin may be oxidized to the harmless stannic form by boiling the HCl solution with 1 ml of HNO_3; the other constituents should then be reduced by boiling with a slight excess of hydroxylamine hydrochloride. The blank should receive the same treatment.

[29] All glassware used in this determination shall be cleaned thoroughly with HNO_3 and rinsed well with water.

capacity. To each funnel, and to an additional funnel for a blank, add enough water to make the total volume about 15 ml. Add 15 ml of the first extraction solution.

(*b*) From a buret, add dithizone solution in 1-ml increments, introducing just enough so that after shaking and allowing the layers to separate, the lower layer has a noticeable purple to green color, which indicates a slight excess of dithizone. From another buret, add chloroform to make the total volume of chloroform and dithizone solution exactly 10 ml. Shake well and allow the layers to separate. Draw off the chloroform layer into a second separatory funnel containing 20 ml of the second extraction solution. Discard the solution remaining in the first funnel. Shake the second funnel, allow the layers to separate, and drain off the chloroform layer into a third funnel containing 20 ml of the second extraction solution. Shake, separate, and draw off a suitable portion of the chloroform layer into an absorption cell. A small plug of cotton may be placed in the tube of the separatory funnel, or the chloroform solution may be filtered on a very small, retentive filter paper, to remove any cloudiness or water. Whatever procedure is adopted should be followed consistently in the preparation of standards and the analysis of samples.

(*c*) Measure the transmittancy or absorbancy at approximately 520 mμ. Compensate or correct for the blank.[30]

(*d*) Plot the values obtained against milligrams of lead per 10 ml of solution.

Procedure

49. (*a*) Transfer a weighed portion of the sample containing 0.1 to 0.7 mg of lead to a 250-ml beaker and add 30 ml of water. Add approximately 20 ml of HCl (1:1) per gram of sample used. When dissolution is complete, heat to boiling and dilute to about 200 ml. Carry a blank[30] through all steps of the procedure, starting with the same quantity of HCl (1:1) and evaporating most of it before diluting.

(*b*) Cool the solution, and transfer to a 500-ml volumetric flask. Dilute to the mark and mix. Transfer a 10-ml aliquot to a separatory funnel. Transfer another 10-ml aliquot to a beaker and titrate with NH_4OH (1:9) until alkaline to methyl red. To the aliquot in the separatory funnel, add 15 ml of the first extraction solution,[31] and as much

[30] The blank color may be due not only to lead but to oxidation products of the dithizone.

[31] If the lead content is low, so that the aliquot taken contains much aluminum, additional ammonium citrate may be required to prevent precipitation of aluminum hydroxide. Since citrate hinders the extraction of lead, as little as possible should be used.

NH_4OH (1:9) as was found necessary to neutralize the free acid in the duplicate portion. Continue in accordance with Section 48 (*b*) and (*c*).

(*c*) Using the value obtained, read from the calibration curve the number of milligrams of lead present in 10 ml of the final solution.

(*d*) *Calculation.* Calculate the percentage of lead as follows:

$$\text{Lead, per cent} = \frac{A}{B \times 10}$$

where,

A = milligrams of lead found in 10 ml of the final solution, and
B = grams of sample represented in 10 ml of the final solution.

CHAPTER 30

ELECTROMETRIC METHODS[1]

In this chapter are presented methods illustrating three aspects of electrometric measurement: (1) measurement of concentration; (2) detection of the end point in titrations; and (3) obtaining of an analytical record of both qualitative and quantitative significance. The methods include the use of potentiometric and polarographic technics.

Potentiometric Methods

DETERMINATION OF ION CONCENTRATION

In the discussion of measurements based on the Nernst equation, it has been assumed thus far that one may use concentration, expressed in moles per liter, as a valid interpretation of the logarithmic term. On this assumption there would seem to be many applications for potentiometric methods of determining the concentration of ions, provided that suitable electrodes that attain equilibrium satisfactorily with the given ions could be formed.

Closer examination reveals difficulties in the method sufficient to render the analytical applications much less promising. Actually, the measured potential depends upon the effective concentration of the given ionic species. This value cannot be expressed in such simple terms as the moles of substance per liter of solution. The effective concentration may be defined as the *activity* of the given species. The activity is related to the concentration by the expression

$$a = \gamma M'$$

where a is the activity, γ is the activity coefficient, and M' is the molality of the species. The activity coefficient may be defined as the percentage

[1] See Chapter 18 for a discussion of this subject.

of the molal concentration that is active. Actually, the above relation applies to unionized substances. In the case of dissociated electrolytes, the activities of the cation and anion are a^+ and a^-, respectively, and ν_+ is the number of positive ions and ν_- the number of negative ions. The mean activity of the electrolyte, $a^{\pm}$, is given by

$$(a^{\pm})^{\nu} = (a^+)^{\nu_+} + (a^-)^{\nu_-}$$

where ν equals $(\nu_+ + \nu_-)$. The activities of individual ions cannot be measured directly but they can be approximated from the mean value for the electrolyte.

The activity coefficient depends on the ionic environment of the solution, including the nature and amount of other ions present (the ionic strength), the temperature, and the dielectric constant of the solvent. The activity of a pure condensed phase such as a pure solid salt is 1, by definition; for this reason the term involving the activity or concentration of a solid species does not explicitly occur in the Nernst equation.

The Nernst equation, then, actually enables the activity of an ionic species to be calculated. The difficulty of evaluating the activity coefficient in a system of any complexity renders the direct calculation of concentration by the Nernst equation somewhat impractical. However, in a solution that is sufficiently dilute, the activity coefficient often can be assumed to be near unity; or the potential values obtained can be correlated with concentration by measurement of solutions of known concentration of active species and of general composition approximating that of the sample solutions to be analyzed. In very dilute solution, such as 0.001 *M* or less, the activity coefficient is assumed to be unity. Its value for most electrolytes then decreases as the concentration increases; for many substances it passes through a minimum value and then increases again.

Exercise 30.1. Determination of Hydrogen-Ion Concentration

The most important and widely used application of the direct potentiometric measurement of concentration or activity is the determination of *p*H. This measurement owes its value to the fact that *p*H control and specification are fundamental for research in almost every area of chemistry, biology, and medicine, as well as for such industrial processes as electroplating, fermentation, water purification, sewage treatment, paper manufacture, and metal pickling.

By definition,

$$p\mathrm{H} = -\log a_{\mathrm{H}^+} = -\log \gamma_{\mathrm{H}^+}[\mathrm{H}^+]$$

where γ_{H^+} is the activity coefficient of the hydrogen ion in the sample

solution. The *p*H of a solution may be calculated from potential measurements using the relations derived in Chapter 18, e.g., using a hydrogen indicator electrode and a calomel reference electrode at 25°

$$p\text{H} = \frac{E_{\text{observed}} + E_{\text{calomel}}}{0.0591}$$

Procedures are subsequently given for the measurement of *p*H using as indicating electrode the hydrogen, quinhydrone, and glass electrodes. In general, the measurements are given more definite meaning by calibration of the apparatus. This is done by measurement of the potential obtained with buffer solutions of known hydrogen-ion activity.[2] If the sample solution has a high ionic strength, calibration of the electrodes used with buffer solutions of comparable ionic strength would be advantageous.

Some potential-measuring instruments can be calibrated to read directly in *p*H values for a given type of electrode combination, e.g., glass and calomel electrodes.

Apparatus

The apparatus required includes a potentiometer, a calomel reference electrode, and the electrode selected for detecting the activity of hydrogen ions. The indicating electrode may be either a hydrogen, quinhydrone, or glass electrode. If the hydrogen or quinhydrone electrode is used, a simple student-type potentiometer is satisfactory. A glass electrode, as discussed in Chapter 18, requires the use of an instrument with vacuum-tube amplification to cope with the high resistance involved in the glass electrode.

Directions are given subsequently for the preparation of electrodes and for the operation of the student-type potentiometer. Directions for the operation of vacuum-tube instruments are usually provided by the manufacturer of the specific instrument involved. The instructor will provide the necessary materials and equipment or will supervise the necessary preparation and assembly.

Preparation of calomel reference electrode. The electrode can be prepared in a vessel such as that illustrated in Figure 18.2 (page 281).

Only materials of a high degree of purity should be used.[3] To prepare

[2] Three such solutions can be formulated from N.B.S. Standard Samples 185 (*p*H 4), 186 (*p*H 7), and 187 (*p*H 9). See Chapter 18.

[3] For directions for the preparation of mercury, mercurous chloride, and potassium chloride see laboratory manuals on physical chemistry, or the works by Bates and Britton, to which reference has been made on page 277.

the electrode, place in the clean container an amount of purified mercury sufficient to insure good electrical contact with the platinum wire in the bottom. Next, cover the top surface with a 6- to 8-mm layer of mercurous chloride made into a paste by rubbing together in a mortar some of the solid with a little mercury and some of the potassium chloride solution to be used. Preferably the latter should be a saturated solution, although both 0.1 *M* and 1 *M* solutions are used. Finally, fill the cell nearly full with the chloride solution and allow enough to run out to fill the side tube. Close the stopcock in the latter. To reduce diffusion of the electrolyte, some cells are fitted with a detachable tip that can be filled with gelatin.

The potentials, referred to the standard hydrogen electrode, of various types of calomel electrodes are given in Chapter 18.

Compact serviceable calomel reference electrodes are commercially available. These are more convenient than those prepared in the laboratory. The potassium chloride solution in vessels similar to that shown in Figure 18.2 should be flushed out at the end of each measurement, to prevent excessive errors arising from liquid-junction potentials at the interface between the potassium chloride solution and the sample solution.

Hydrogen electrode. The hydrogen electrode (Figure 30.1) consists of a small rectangular piece of platinum fastened to a wire sealed through a small glass tube. The inside of the latter contains mercury or some other means of making contact with an external connecting wire. The whole unit is surrounded by a tube arranged so that hydrogen gas can be passed over the electrode surface. The electrode surface must be coated with platinum black before use.

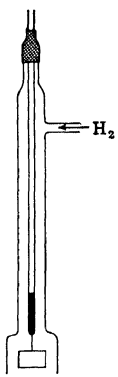


Figure 30.1

Hydrogen electrode

Before "platinizing" the smooth foil, clean it with hot chromic acid solution. Then immerse the foil in a beaker containing 2 per cent platinic chloride and 0.02 per cent lead acetate. With a platinum wire for the other electrode, an ammeter, an adjustable resistance and a double-pole double-throw switch in the circuit, pass a current of about 0.05 amp. through the solution. By means of the switch, reverse the current every half-minute. Continue the electrolysis for about 5 min., or until a thin, velvet-black deposit covers the foil. Replace the bath with one containing very dilute sulfuric acid and continue the electrolysis for 15 min. Remove the foil, wash thoroughly, and place

in distilled water until the electrode is to be used. To remove the deposit, immerse the foil for a few seconds in warm aqua regia.

Before use, such an electrode is washed well with water and then placed in the solution to be measured. It is saturated with hydrogen by passing purified hydrogen into the opening shown in Figure 30.1 and allowing the gas to bubble slowly through the solution surrounding the electrode. As a source of hydrogen, the student may use the best grade of compressed gas, which should be purified by passing it successively through bubbling towers containing 5 per cent solutions of alkaline pyrogallol, potassium hydroxide, potassium permanganate, and, finally, pure water.

Glass electrodes. Glass electrodes are available from any of the usual supply houses in two types: (1) general-purpose electrodes, usable up to *p*H 10 or 11; and (2) alkali-resistant electrodes for the *p*H range of 9 to 14. However, it is possible to make serviceable glass electrodes in the laboratory.

To prepare a glass electrode, first blow a *thin* bulb about 2 cm in diameter on the end of a piece of Corning No. 015 glass tubing. Cut a 15-cm piece of 12-mm-bore soft glass tubing, with one end smooth and square. Heat this until it is soft and begins to contract. Press the red-hot end against the bulb of No. 015 glass. The heat is sufficient to fuse the membrane in place.

As the internal reference electrode, Dole[4] recommends the silver-silver chloride combination in a chloride buffer. The electrode may be prepared by electrolyzing a dilute solution of hydrochloric acid for a few minutes at 0.03 amp. with a silver wire anode.

As an alternate, quinhydrone is quite satisfactory. It must be renewed every few days, but that operation is simple. The glass electrode is filled to a depth of about 1 cm with 0.1 *M* hydrochloric acid saturated with quinhydrone. A platinum wire is heated to redness for cleaning and immersed in the acid.

Potentiometer. The principle of the potentiometer and its use in precise potential measurement are discussed in Chapter 18, where the wiring diagram of the usual student-type potentiometer is reproduced. The working arrangement of the potentiometer and the necessary accessories are given in Figure 30.2. In this circuit, *R* is a 999.9-ohm decade resistance, *K*-1 and *K*-2 are tapping keys, *P* is a 10,000- to 100,000-ohm resistance, and *G* is a box and lamp-scale galvanometer of about 0.03 microamps. per mm sensitivity.

[4] *The Glass Electrode,* p. 98, Wiley, 1941.

Before making any potential measurements, the student must calibrate the slide wire in the potentiometer circuit against the standard cell as follows: Throw switch S (Figure 30.2) to the standard-cell position. Then turn dial switch A and knob B until the potentiometer reading corresponds to the potential of the standard cell being used. Set the adjustable rheostat R at approximately 140 ohms to give approximately 0.01 amp. through the potentiometer circuit. Then press and release K-1 and at the same time note the galvanometer deflection. Adjust R to reduce any deflection of the galvanometer. Again tap and release K-1 and note the deflection. Repeat this procedure until the galvanometer deflection is zero or very small. Then press and release K-2 and make final adjustment of R until the galvanometer does not deflect when K-2

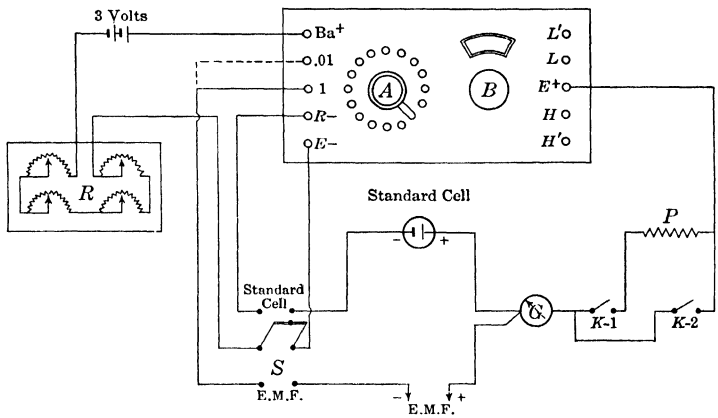


Figure 30.2

Leeds and Northrup student potentiometer circuit.

is closed. The potentiometer is then ready for making measurements. It is advisable to check the potentiometer circuit occasionally to be sure that no change occurs. To do this, throw the switch to the standard-cell position and press K-2. Adjust the rheostat R, if necessary, to balance the galvanometer at zero.

To measure an unknown emf, throw switch S to the sample-cell (emf) position. Press K-1 and note the galvanometer deflection. Reduce the deflection by adjusting A and B. Then press K-2 and adjust B until the galvanometer balances at zero. The sum of the readings on dial A and the slide-wire scale over B will give the value of the potential being measured. The reading is in volts when the 1.6-volt range is being used. When the 16-millivolt range is being used the reading must be multiplied by 0.01 to get the value in volts.

If a vacuum-tube *p*H meter is to be used, operating directions will be provided in the manufacturer's instructions.

The Sample

Secure enough of the aqueous solution, the *p*H of which is to be measured, to fill the vessel in which the electrodes are to be immersed to an adequate depth (*1, 2*). In some cases, provision of some sample solution for a preliminary rinsing of the electrodes may be necessary.

The Desired Constituent

Measurement. Assemble the apparatus to be used (student-type potentiometer circuit or vacuum-tube meter) and become familiar with its operation. Specific operating directions will be furnished, if necessary.

Insert the indicating electrode in the sample solution (*3*) and immerse the tip of the calomel reference electrode below the surface of the solution. Determine the potential difference for the specific electrode combination used.

The method of calculating the hydrogen-ion concentration (activity) or the *p*H of the solution from the observed potential has been discussed in connection with the description of each indicating electrode in Chapter 18.

NOTES: (1) For small amounts of liquid, various special electrode vessels have been designed. See the books by Bates or Britton (cited on page 277) for details of such vessels.

(2) This determination is an example in which no definite quantity of sample is required.

(3) If the hydrogen or quinhydrone electrodes are used, the hydrogen supply must be suitably regulated or the quinhydrone added to saturate the solution.

DETECTION OF END POINTS IN TITRATIONS

The preceding section has been devoted to the technic of obtaining electrode potentials and of applying such measurements to the determination of activity (or estimation of concentration) by means of the Nernst equation. The application of the method was illustrated by the use of various types of indicator electrodes for determination of *p*H values.

Another application of this method is in so-called "potentiometric titration" which is actually a method for indicating the location of end points in the use of different types of titrimetric measurements.

Titrations are accompanied by a change in concentration of (at least) the ion reacting with the titrant, as well as by an increase in concentration of the titrant component itself once the equivalence point has been passed.

In order to follow the course of the reaction, the analyst must have available an electrode that is in equilibrium with the ion concerned. As previously discussed, the potential of this indicator electrode can be determined by measuring the potential difference between it and a known reference electrode. At 25°, the measured potential of the cell will vary, according to the Nernst equation, by $0.0591/n$ volts for each tenfold change in concentration of the ion being titrated.

While most potentiometer assemblies allow only the potential in volts or millivolts to be measured, instruments can be calibrated to read directly in units of $-\log$ [ion]. The latter alternative is most useful for hydrogen-ion measurement, in which case *p*H values are determined directly. Actually, commercial *p*H meters are calibrated to read directly in *p*H units.

From the concentrations at the equivalence point the potential to which one should titrate for a desired end point may be calculated. However, this procedure is neither common nor necessary except for very special situations. We are actually interested in following the change in ion concentration. The relative change of potential with volume of titrant is the best indication of the equivalence point. For example, the point of stoichiometric neutrality in the titration of a strong acid with a strong base should be *p*H 7. The more common practice is to plot the potentials or *p*Ion values, usually as ordinates, against the volumes of titrant, usually as abscissas. As the equivalence point is approached, an increasing change in potential is observed for a given increment of titrant. When the equivalence point is passed, the changes decrease again. The curve obtained then shows a marked "break" at the equivalence point, as illustrated in Figures 13.2 and 13.3 (page 205) for neutralization reactions. The end point is taken as the mid-point in the steepest vertical portion of the curve. Dropping a perpendicular from this point to the base line indicates the volume of titrant required to complete the titration.

Similar curves are obtained for other reactions, such as those involving oxidation-reduction or precipitation. In neutralization titrations, *p*H is usually taken as the ordinate. The reason that potentials may be plotted directly as a measure of concentration is owing to the fact that the potential of the Nernst equation varies directly as the log of the concentration. For example, the measured potential [5] for a given titration would be given by

[5] The convention of signs used in this book for electrode potentials requires that a negative sign be used on the observed potential in the formulas whenever the reference electrode is negative with respect to the indicator electrode

$$E_{\text{observed}} = E_{\text{indicator}} - E_{\text{reference}}$$

$$= E^0_{\text{ind}} - \frac{0.059}{n} \log [\text{Ion}] - E_{\text{ref}}$$

$$= E^0_{\text{ind}} - E^0_{\text{ref}} + \frac{0.059}{n} p\text{Ion}$$

Since E_{ref} and E^0_{ind} are unchanged during the titration, the observed potential will vary linearly with the logarithm of the concentration. Since the volume of the titrant added is a measure of the change of concentration of the desired constituent in the sample solution, the plot of potential versus titrant volume on the usual linear co-ordinate scale gives an S-shaped curve, as discussed in Chapters 13 to 15.

Instead of a curve co-ordinating potential or pIon, e.g., pH in neutralization titration, and volume of titrant, the change in potential or pIon per unit increment of titrant may be used as the ordinate. This use of the first derivative of the potential change with extent of reaction affords greater sensitivity in the detection of the equivalence point, since the resulting curve then resembles that in Figure 30.3, which shows a maximum at the point of greatest change. The latter point corresponds to the sudden vertical rise in the usual plot.

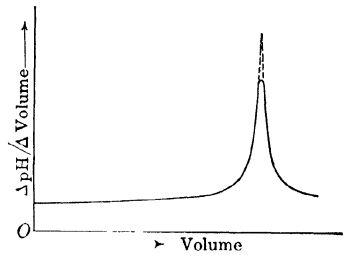


Figure 30.3

Differential plotting of end point.

The magnitude of the ratio $\Delta E/\Delta V$ is dependent on the concentration and the reactivity characteristic of the constituent being titrated, e.g., the ionization constant for acids. The larger the ionization constant, the greater the relative change. Only certain systems, such as the formation of uniunivalent compounds (as in the precipitation of silver chloride), give symmetrical curves. A perpendicular dropped from the peak to the base line gives the volume of titrant used. This method is, obviously, less uncertain with regard to selection of the point from which to draw the perpendicular line. Still greater accuracy may be obtained by finding the point where the second derivative, $\Delta E^2/\Delta V^2$, equals zero.

When the breaks in such curves are used as an indication of the location of the end point, the requirements of accuracy in obtaining true potential measurements are not exacting. Thus, although the end point would not be changed if the curve were simply moved up or down somewhat, the

ionic concentration indicated by any individual point would not be accurate.

The exercises given below contain directions for obtaining the end point potentiometrically for three representative titrations.

Exercise 30.2. Titration of an Acid (or Base)

Since the titration of an acid or base requires that the change in concentration of the hydrogen ion be followed, the analyst has a choice of indicating electrodes, particularly the hydrogen, quinhydrone, or glass electrodes. The quinhydrone electrode suffers the limitation of being unreliable much above *p*H 8. Since the hydrogen electrode is less easily handled than the glass electrode, the use of the latter is described here.

The Sample

Selection. Select a sample of a suitable acid or base (*1*).

Measurement. Transfer a convenient amount, such as 25.00 or 50.00 ml, to a clean 250-ml beaker and dilute the solution to about 100 ml.

If a solid or liquid sample is to be analyzed, a measured portion (mass or volume) can be similarly diluted; or it can be diluted to a given volume and an aliquot taken.

The Desired Constituent

Measurement. Insert the glass and calomel electrodes in the beaker and connect them to the measuring instrument. Provide, if possible, a mechanical or magnetic stirrer for the solution. Arrange the buret to deliver the titrant into the beaker. Determine the *p*H or *E* before any titrant is added. Then add 2 ml of titrant (*2*) and repeat the measurement.

Record the data in columns, with buret readings opposite the corresponding instrument readings. Continue the additions of titrant and readings of *p*H or *E*. When the change in *p*H or *E* per increment of volume becomes larger, i.e., when the rise in the titration curve becomes more pronounced, add smaller amounts of titrant. In the region of the equivalence point, where there is the greatest change of *p*H or *E* per titrant increment, add the titrant a drop at a time (*3*).

If the sample gives more than one equivalence point, e.g., contains soda ash or a mixture of alkaline or acidic constituents, the same general manner of data-gathering is repeated.

Calculation. Construct a curve co-ordinating *p*H or *E*, as ordinate, with volume of titrant, as abscissa. From the mid-point of the nearly

vertical portion, or "break" in the curve, determine the volume of titrant required to react with the desired constituent.

Verify this figure by constructing the differential curve, $\Delta p\mathrm{H}/\Delta V$ *vs* V, for the volume region of about 1 ml on either side of the end point. Calculate the concentration of the solution titrated, or the percentage of desired constituent, if desired.

NOTES: (1) The discussion in Chapter 13 indicated that potentiometric curves show the most satisfactory breaks for acids and bases having ionization constants greater than 10^{-5}.

(2) If desired, initial readings may be confined to each 5 ml.

(3) It is instructive to add an indicator, such as methyl orange or phenolphthalein, and note the $p\mathrm{H}$ range through which it undergoes its color change.

Exercise 30.3. Titration of a Reductant

As previously discussed (Chapters 14 and 18), the potential at 25° of an indicator electrode, such as platinum, in contact with a solution of a substance present in two different oxidation states may be expressed as

$$E = E^0 - \frac{0.0591}{n} \log \frac{[\text{red}]}{[\text{ox}]}$$

which is based on the equilibrium

$$\text{Ox} + ne \rightleftarrows \text{red}$$

As ferrous iron is titrated with a suitable oxidant, for example, there will be a continuous change in the ratio, $[\mathrm{Fe}^{+2}]/[\mathrm{Fe}^{+3}]$, and, consequently in the magnitude of the measured potential E. By measuring the relative change in E versus a reference electrode, the analyst may secure data for plotting a characteristic titration curve with E as ordinate and of volume of titrant as abscissa.

Many substances capable of undergoing oxidation-reduction can be titrated in this manner. The method given here is for iron. If the material is to be oxidized and is not already in the lower state of oxidation, it must first be reduced.

Apparatus

An ordinary potentiometer may be used, with calomel and platinum electrodes. The Hildebrand assembly, illustrated in Figure 18.7 (page 288), is a simpler apparatus, and is suggested for this determination.

The Sample

Selection. Select an iron ore (*1*), such as that used in Exercise 26.6 for estimation by titration with dichromate.

Measurement. Follow the directions given in Exercise 26.6 for the measurement and preliminary treatment of the sample, except for the substitution of a 250-ml beaker for the 500-ml conical flask.

The Desired Constituent

Measurement. Arrange the platinum and calomel electrodes of the potentiometric assembly in the beaker containing the reduced iron, together with a stirrer and a buret for delivering the titrant. Perform the titration as directed in the previous exercise.

Plot the titration curve and determine the end point in the same way as for a neutralization reaction (*2*). Calculate the percentage of iron.

NOTES: (1) Experience in using this method for determining end points can be secured just as well by titrating an acidified solution of ferrous ammonium sulfate. (2) What would be the effect of omitting the solution of mercuric chloride? Could the iron still be titrated potentiometrically? (One sample should be tried in this way.)

Exercise 30.4. Titration of a Precipitant

In Chapter 15, mention was made of the possibility of determining potentiometrically the equivalence point for the titration of chloride ion with a solution of silver nitrate. A silver electrode may be used for following the silver ion concentration through the course of the reaction. The silver ion concentration is related to the chloride ion concentration through the solubility-product constant for silver chloride.

The data may be plotted as in the previous methods, the ordinate having either observed potential or *p*Ag value. The latter may be calculated at 25° from the relation

$$p\mathrm{Ag} = -\log [\mathrm{Ag}^+] = \frac{E_{\text{observed}} - E_{\text{reference}} + E^0_{\mathrm{Ag}^+/\mathrm{Ag}}}{0.0591}$$

Apparatus

The apparatus is the same as that suggested for determining hydrogen-ion concentration except that, instead of using a hydrogen or quinhydrone electrode, a silver electrode is substituted. It may be a silver wire, or a platinum wire plated with silver (*1*), sealed into a glass tube like the electrode used for oxidation-reduction titrations. Since chloride is to be determined, the sample vessel in which the silver indicator electrode is immersed is connected by a salt bridge containing potassium nitrate to a vessel in which the calomel reference electrode is immersed.

The Sample

Selection. Use a sample similar to that suggested in exercise 27.4 for the titration of chloride by means of silver nitrate and an indicator compound.

Measurement. Follow the directions of Exercise 27.4 for the measurement and preliminary treatment of the sample.

The Desired Constituent

Measurement. Proceed with this titration as directed for the potentiometric titration of an acid (Exercise 30.2).

Plot the data in the usual way. From the volume of silver nitrate used to reach the end point, calculate the percentage of chloride.

NOTES: (1) To plate an electrode with silver, immerse the platinum wire in a solution of silver nitrate (about 0.1 *M*) to which enough potassium cyanide has been added just to dissolve the precipitate that forms at first. A substantial deposit should be obtained with the current set at not more than 0.1 amp. When sufficient silver is deposited, the electrode should be washed free of adhering solution.

Polarographic Methods

Polarographic technics can be used for the three general purposes for which electrometric technics are suitable: (1) determination of the concentration of an electroreducible or electro-oxidizable species; (2) location of the end point in a titration; and (3) obtaining of an analytical record possessing both qualitative and quantitative significance. The first and third topics are usually discussed under the general heading of polarographic analysis, whereas the second topic is segregated under the name of *amperometric titration.*

POLAROGRAPHIC ANALYSIS

The basis for quantitative polarographic analysis, as discussed in Chapter 18, is the usually linear relation between concentration and diffusion current. In many cases the concentration of a certain constituent in a sample may be determined by comparing the diffusion current resulting from that constituent in a solution of the sample in a given medium, to the diffusion current of a known amount of the same constituent in the identical medium and under identical experimental conditions. If the linearity of the relation is in doubt or somewhat greater accuracy is desired, the standard-series technic may be used to establish the relation

between current and concentration. The Ilkovic equation or the internal standard ("pilot ion") technic may also be used as the basis of methods of quantitative polarographic analysis.

Measurements of concentration made polarographically have, generally, a precision of from 1 part in 30 to 1 part in 100, a precision comparable to that of a number of other methods. With great care, on the part of the analyst, better precision and accuracy are possible.

Qualitative analysis using polarographic technics is of limited applicability since half-wave potentials must be at least 0.10 to 0.15 volts apart in order for the waves to be separated. In general, the technic is used in a negative sense, that is, the failure of a wave to appear is used to verify the absence of a constituent. The variation of the half-wave potential with composition of the solution may be helpful in identifying a species in solution or in separating the waves caused by different species. This shift is due to complexation of the ion or the pH of the solution. The resultant shift of the half-wave potential is analogous to the manner in which the standard electrode potential is changed. Common complexing electrolytes include solutions of cyanide, oxalate, citrate, tartrate, fluoride, and phosphate salts.

A variety of polarographs, suitable for different types of measurement, are commercially available. The manual polarographs consist essentially of a slide-wire for taking off a variable potential to be applied to the microelectrode, and a galvanometer for indicating the current, together with accessories for calibrating the slide-wire, varying the galvanometer sensitivity, reversing the polarity, and making the apparatus more flexible and useful.

The automatically operated polarographs are of two general types. The variation of the potential selected from the slide-wire by a motor-operated contact is synchronized with the movement either of (1) a drum carrying a sheet of photographic paper wound around it or (2) the paper roll in a strip-chart recorder. In the former type, the current is recorded by the deflection of a galvanometer beam across the paper perpendicular to the direction of rotation. In the strip-chart recorder type, the current is marked by the inked track of a pen moving perpendicular to the direction of movement of the chart paper. In the latter type, the current may be passed through a standard resistance and the resulting potential drop measured by the recorder.

The manual apparatus is generally capable of equal or better accuracy or measurement, as compared to the recording instruments. For student use or for the most precise research measurement, a regular potentiometer

arrangement is advised. The description of the assembly and use of such an apparatus is given.

The operational procedure of commercial polarographs will be found in the directions supplied by the manufacturer. Details for the operation of several commercially available polarographs are given by Willard, Merritt, and Dean.[6]

The "student" polarograph described is based on one recommended by Lingane.[7] It is very inexpensive, involving only two (readily available) parts with a few common minor items, plus a student-type potentiometer. The schematic electrical circuit is given by Lingane in the reference cited.

The wiring diagram for this polarograph is given in Figure 30.4. R_1 is a 100-ohm radio-type potentiometer such as the General Radio Company, Type 214-A, equipped with a General Radio Co., Type 318-D, dial

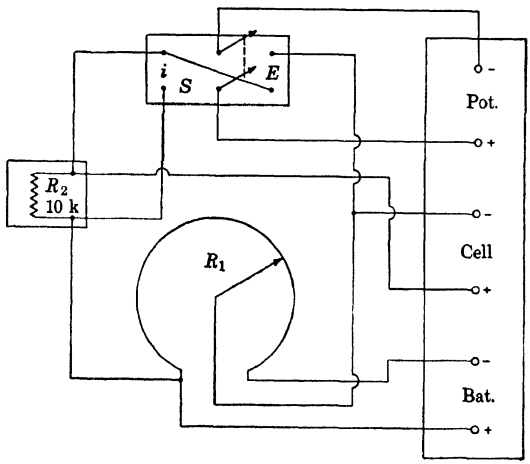


Figure 30.4

Wiring diagram of polarograph

plate. R_2 is a 10,000-ohm precision fixed resistance such as the General Radio Co., Type 500-J. S is a double-pole double-throw switch that enables either the potential applied to the polarographic cell or the current flow to be measured by the external potentiometer. Three sets of two binding posts each are indicated for connection to two 1.5-volt dry cells in series (*bat*), to the polarographic cell (*cell*), and to the external potentiometer (*pot*). The binding posts are not necessary, since connec-

[6] Willard, Merritt, and Dean, *Instrumental Methods of Analysis*, Van Nostrand, 1951.
[7] Lingane, *Anal. Chem.* 21, 47 (1949).

tions may be made directly to the terminals of R_1, R_2, and S. These three items are conveniently mounted on a board to which the binding posts and dry cells may also be fastened. The potentiometer R_1 is best mounted on a piece of metal bent at an angle of about 60° and fastened to the board.

The polarographic potentiometer R_1 is used to vary the applied potential. It is adjusted to sweep the complete dial-plate scale from 0 to 10. It may be calibrated as follows: With 1.5 volts across it, determine the potential to 1 millivolt at six settings of the dial (the potential is measured with the external potentiometer). Repeat, using an applied potential of 3 volts; the external potentiometer will have to be set to double its usual range. Plot the data. The measuring resistance R_2 can be checked by a Wheatstone bridge measurement. The polarographic current is measured in terms of the iR drop across this resistance, as reflected in its measurement by the external potentiometer.

Any ordinary potentiometer may be used as the external measuring potentiometer; the student potentiometer, as indicated, serves very well. The galvanometer used with it should be damped by placing a resistance across its terminals so that the oscillations resulting from growth and fall of the mercury drop at the electrode do not extend over more than 1 or 2 cm of the scale. The potentiometer has been brought to balance when the oscillations extend an equal distance on either side of the galvanometer scale zero.

Another student polarograph is described in the reference cited by Willard, Merritt, and Dean.

The dropping mercury electrode is the most widely used polarizable microelectrode. A convenient electrode assembly consists of a 3- to 8-in. length of capillary bore (about 0.02 to 0.05 mm) glass tubing, 80 cm of clean, sulfur-free, and metal-free tubing (Tygon is good), and a 125-ml leveling bulb.

The most satisfactory and rugged capillary is a piece of marine barometer tubing. Less satisfactory capillaries may be made by heating and drawing pieces of thermometer tubing. The length is determined by trial and error, i.e., by successive decreases in length, so that the capillary will give a drop life of about 5 sec. when immersed in water with a head of mercury of 30 to 80 cm. The end of the capillary should be flat. Capillaries can be selected with predetermined characteristics.[8]

Only pure mercury should be used. Electrical connection to the mercury in the leveling bulb should be made with a piece of platinum wire or other metal that will not dissolve in the mercury.

[8] Müller, *Anal. Chem.* **23**, 1175 (1951).

A rotating platinum microelectrode is advantageous in amperometric titration. An adequate one consists of a 3-mm piece of wire, 0.05 mm in diameter, projecting from a glass tube the end of which is bent and curved so that the glass sweeps the solution before it comes in contact with the wire. Such an electrode serves to stir the solution. A speed of about 500 r.p.m. is adequate. Connection to the electrode may be made through a wire running inside the tube from the platinum to the motor chuck. The currents obtained with such an electrode are many times that of the average dropping mercury electrode, often being 100 times as large.

The reference electrode may be a saturated calomel electrode similar to that used in potentiometric measurement, if it has a low resistance. In many cases, a mercury pool serves as a reference electrode, as discussed in Chapter 18. Many *H*-type cells for polarographic work, which include a reference electrode built into one arm of the *H*, have been described. Examples of such cells are illustrated in the references previously cited.

Exercise 30.5. Analysis of Polycomponent Sample

As discussed above, the basis for polarographic quantitative analysis is the linear relation of concentration and diffusion current. In addition, qualitative information is available from the fact that the half-wave potential of a substance is a characteristic value for a given solution composition and temperature.

Apparatus

All work involving mercury must be done in a tray with adequately high sides. If any mercury is spilled, it must be cleaned up immediately. Gold jewelry should not be worn where it may come in contact with mercury.

Set up a dropping mercury electrode (D.M.E.) assembly consisting of a 125-ml leveling bulb, 30 inches of neoprene or Tygon tubing, and a suitable capillary or marine barometer tubing (drop-time t of 4 to 6 sec. at open circuit). Wire the glass-to-rubber connections.

Mount the assembly on a tall ring stand. Arrange the capillary in such a manner that its position relative to the head of mercury is reproducible. Mark the intended mercury level on the bulb with a label (at widest portion of the bulb; why?). Provide a test tube with about 1 cm of mercury in it for protecting the capillary when it is not in use (a capillary clogged by a piece of dirt is usually impossible to clean); mount the

tube a few inches below the bulb mercury level. Whenever the capillary is not in use, the tip should be kept immersed in mercury at a reduced height.

Fill the assembly with mercury to the mark; be sure the mercury drops freely from the capillary.

With the capillary immersed in a test-tube of 0.1 *M* potassium chloride and with the head of mercury, *h*, at 40, 60, and 80 cm, measure the time (with a stopwatch) required for the formation of 10 drops. The preferred drop-time is between 4 and 6 sec. under open-circuit conditions. Use a height that corresponds to about 5 seconds drop-time (*t*); note this height (lower tip of capillary to mercury level in bulb). What is the relation between *h* and *t*?

Transfer all used mercury to the waste-mercury bottle provided. Mercury, as well as its vapor, is poisonous and must be handled carefully.

Assemble and connect the parts for a manual polarograph as directed by the instructor, or familiarize yourself with the directions for the polarograph furnished. Calibrate the potential-setting device and current-indicating arrangement as necessary.

The Sample

Selection. The sample solution may contain any or all of the group of cadmium, copper, lead, and zinc ions in the concentration range of 10^{-2} to 10^{-4} *M*. If it is more concentrated, dilute to this range.

Measurement. Dilute 10.0 ml of this sample with 50.0 ml of 0.10 *M* potassium chloride and transfer to a 125-ml conical flask or other suitable polarographic cell.

The Desired Constituent

Measurement. Insert the dropping mercury and the saturated calomel reference electrodes in the cell and connect the electrodes to the polarograph (*1*).

Remove dissolved oxygen from the solution by inserting a glass tube connected to a nitrogen source (*2*) and bubbling nitrogen through the solution for 15 min. Then raise the tube above the surface of the solution so that a blanket of nitrogen is maintained to exclude air.

Determine the current-potential relation from 0.00 volts *versus* the reference electrode to about -1.9 volts, where the potassium ion of the background electrolyte begins to be electrolyzed. Take readings at intervals of about 0.05 volts, using larger intervals when on the flat portions of the curve and smaller intervals, if desired, when the current increases occur (*3*).

Calibration and calculation. Determine in a similar manner the *i-E* curve for the base solution itself, i.e., for 0.1 *M* potassium chloride solution. Readings need be taken no closer than intervals of 0.1 volt.

Determine similarly the *i-E* curve for a standard solution containing the four possible ions in a comparable concentration range. The waves appear in the order: copper, lead, cadmium, zinc.

Plot the data (see Figure 18.12, page 293) for the sample and standard solutions on separate sheets of graph paper (*4*). Calculate the diffusion currents and half-wave potentials for each step, by the intercept method.

Using a straight-edge, draw straight lines through the "flat" portions before and after each current step. Through each point of intersection, draw lines parallel to the potential axis.

The step-height in each case, i.e., the vertical distance between the two parallel lines limiting the wave, is the diffusion current.

Bisect the vertical distance thus found for each wave. Extend to the current step, or wave, a line parallel to the potential axis. From the point of intersection thus obtained, drop a perpendicular to the potential axis. The location of the latter point of intersection is the half-wave potential.

From the wave-heights or diffusion currents for the known and unknown concentrations of each ion and the concentrations of the ions in the standard, calculate the concentrations of the ions in the sample solution. Using the dilution information, calculate the percentage or other type of composition of the original sample.

NOTES: (1) A pool reference electrode and simple polarographic cell may be made by adding sufficient mercury to cover the 2 or 3 mm of platinum lead wire inserted through the bottom of a large (about 1-in. in diameter) test-tube.

(2) Tank nitrogen may be purified by successive passage through bubblers containing alkaline pyrogallol solution, sulfuric acid solution, water, and some of the background solution (0.1 *M* potassium chloride solution).

(3) If the waves merge, i.e., if the flat portions between the individual steps are poorly defined, repeat the measurement after a further five- or tenfold dilution of the sample with 0.1 *M* potassium chloride solution.

(4) Correction of each current value for the residual current as found for the base solution may be advisable.

AMPEROMETRIC TITRATION [9]

In using the polarographic technic to locate the end point in a titration, a potential is applied to the indicator microelectrode which corresponds to a point on the limiting current portion of the polarographic wave that

[9] This term is unfortunate in that the unit of measurement, rather than the property measured, is involved.

would be given by the substance to be determined, the titrant, or both. In the first case, as the constituent being titrated is removed from the solution (e.g., precipitated) the current decreases to zero, except for the residual current effect. In the second case, the current is almost zero until the end point is reached, and then increases as excess titrant is added. Where the applied potential is sufficient to reduce both substances, the plot of current *versus* volume of titrant is V-shaped.

In such amperometric titrations, as in conductometric titrations, the taking of many current readings is unnecessary. By taking several readings on either side of the equivalence point, the student will be able to locate two straight lines the intersection of which marks the end point. In plotting the data, he should correct each current reading for the effect of dilution, as follows:

$$i_{(\text{corr.})} = \frac{V + V'}{V} \times i_d$$

where i_d is the current measured, V is the original solution volume, and V' is the volume of reagent added. The rounding-off of the point of intersection observed in practice is owing to the solubility of the precipitate which increases the ion concentration at the equivalence point.

Amperometric titration has been most successful in titrations involving precipitation, although interesting applications to redox titrations have been made.

In some such cases, the necessary applied potential may be obtained by using as a reference electrode a system the potential of which is much more negative than that of the calomel electrode. By simple connection of the two electrodes through a galvanometer (or other current-measuring device), the potential impressed on the polarizable microelectrode is actually that of the nonpolarizable reference electrode.

Exercise 30.6. Determination of Lead

Apparatus

A manual polarograph, such as that suggested for Exercise 30.5, is well suited for this purpose.

The Sample

Selection. Any of the common soluble salts of lead may be used (*1*).

Measurement. Measure an amount of the sample to give, when diluted to a definite volume, a solution that is about 5 millimolar in lead ions. Dilute 10.0 ml of this solution with 50.0 ml of 0.10 *M* potassium nitrate and add 0.2 ml of 2 per cent gelatin solution (*2*).

Transfer a portion, or all, of this solution to the titration vessel, e.g., a 250-ml beaker.

The Desired Constituent

Measurement. Insert the dropping mercury and calomel electrodes in the titration cell and connect them to the polarograph. Apply to the dropping mercury electrode a potential of −1.0 volt versus the saturated calomel electrode.

Oxygen need not be eliminated in this experiment (*3*). Measure the diffusion current of the lead nitrate solution at a sensitivity which gives nearly full-scale galvanometer deflection or corresponding iR-drop value.

Add 0.025 M potassium dichromate solution from a micro buret in 0.1-ml portions, stirring vigorously after each addition (a stream of air may be used for this purpose). Allow the solution to become perfectly still before taking a new current reading. After the end point has been reached, continue titrating until the initial deflection is again nearly attained. Draw straight lines through the two sets of points. The point of intersection indicates the volume of titrant required.

For a perhaps more accurate value, use the corrected current values in plotting a current-volume curve; indicate the end point; calculate the concentration of lead in the sample solution. From this concentration and the dilutions of the original sample, the lead content can be calculated.

NOTES: (1) If necessary, the lead can be converted to a soluble form by suitable fusion or extraction procedures. The *p*H of the sample solution should be about 4.

(2) The purpose of the gelatin is to eliminate so-called "maxima," which are undesirable current surges or increases.

(3) If oxygen is removed, the solution may be stirred with the nitrogen stream.

Exercise 30.7. Determination of Mercaptan

Mercaptans are organic compounds which are the sulfur analogs of the alcohols and have the general formula RSH, where R represents an alkyl group. The hydrogen atom in the mercaptan grouping is ionizable; the mercaptan is a weak acid.

Mercaptans may be determined [10] by a simple, accurate, and rapid amperometric titration with standard silver nitrate solution, using a rotating platinum microelectrode and a suitable reference electrode (mercuric iodide). The electrodes are connected through a galvanometer or microammeter without the application of an external potential. The current is measured at the potential of the platinum microelectrode, essen-

[10] Kolthoff and Parks, *Ind. Eng. Chem., Anal. Ed.* **18**, 161 (1946).

tially that of the reference electrode, the potential of which is −0.23 volts versus the saturated calomel electrode.

Apparatus

Use an instrument of the type suggested for Exercise 30.6.

The Sample

Selection. For this exercise, use some substance such as duodecyl mercaptan.

Measurement. Measure an amount of sample to give, when diluted to a definite volume, a solution each milliliter of which contains the equivalent of about 0.6 mg of mercaptan sulfur. Dilute to the selected volume with 95 per cent ethanol.

Transfer 5.00 ml of this solution to a 250-ml beaker and add 55 ml of 95 per cent ethanol. Make the solution 0.25 *M* in ammonia and 0.5 *M* in ammonium nitrate.

The Desired Constituent

Measurement. Immerse in the sample beaker the rotating platinum electrode and the salt-bridge connection to the reference electrode (*1*). Connect the two electrodes through a microammeter (50 ma) equipped with a variable-sensitivity shunt.

Titrate with aqueous 0.005 *M* silver nitrate. Take two or three readings of the microammeter before and after the end point. If necessary, change the sensitivity of the current indicator and correct accordingly. If the current response becomes sluggish, clean the platinum electrode by wiping with a clean cloth (*2*). If clear readings are not obtained, repeat the experiment and omit the ammonia.

Plot the titration curve and determine the end point as in the preceding procedure. Correct for dilution. Calculate the percentage of mercaptan sulfur or of specific mercaptan, if known.

NOTES: (1) The preparation of the salt-bridge and the mercuric iodide reference electrode are described in the reference by Kolthoff and Parks, previously cited. When not in use, the salt-bridge should be immersed in saturated potassium chloride solution; it should be rinsed with distilled water before use.

(2) A new or freshly cleaned electrode may give an abnormal current which disappears in a few minutes.

CHAPTER 31

ANALYSIS OF SELECTED INDUSTRIAL MATERIALS

Every day, many thousands of determinations are made on samples in which the amount of *some single constituent* is the important information sought. Thus, in the steel industry, the composition of the charge for the blast furnace is based primarily on the iron content of the ore. Another example is the determination of butterfat in milk to ascertain whether the sample meets state or municipal requirements. The exercises included in the preceding chapters were selected to illustrate the application of a variety of methods of separation and measurement for the determination of such components in typical products.

Of equal industrial importance is the general analysis of materials containing *several constituents*. Such work involves the determination of all the constituents of interest for a given purpose. In a granite rock, for example, as many as twenty or more constituents may be required.

If a complete analysis is to be made, the general analytical approach usually depends to some extent upon the relative amounts of the desired constituents. In the analysis of water or steel, for example, the material is, respectively, water or iron more or less contaminated with other constituents that are considered minor, at least with respect to their relative amounts. In these two examples, neither of the major constituents is determined. If reported at all, their amount is taken by difference. This practice of determining minor constituents is quite general; the main reason for it is that the uncertainty of the error in the determination of a major constituent such as water may exceed or approach the total amount of the minor constituents. The alternative method is to determine *all* the constituents, as in bronze, a copper-base alloy. Here, although the proportion of copper, the major constituent, varies widely (often from 50

to more than 95 per cent), it is regularly determined, along with the other constituents.

In the complete ultimate or elemental analysis of organic compounds, the practice for over a century was to determine all of the elements present except oxygen. The oxygen was then generally calculated by subtracting the total of the percentages of the other elements from 100. The reason for this practice, which threw all of the uncertainty of several determinations on the value for oxygen, was lack of a satisfactory method for determining oxygen in organic compounds. This long-standing problem has finally been overcome.[1]

The procedures recommended in compilations of industrial and official methods[2] consist of a variety of operations for separation and measurement. Important factors involved in the establishment of the methods are enumerated in the discussion of the library problem in Chapter 32. Since there are often several possibilities for the separation and measurement of a constituent, the method specified in a given procedure is not necessarily "the" method. It may be generally preferable as given, but it may also represent personal preference. Usually in such work the analyst uses the combination of separations and measurements that is most feasible for the given situation which may include such factors as personnel, equipment, nature of the material, time available, and quality of results needed.

The methods recommended in compilations of official methods are usually the results of co-operative study. They represent the optimum procedures for the determinations specified, as found by a large number of analysts in different laboratories.

In order to provide an introduction to this kind of practical analytical work, several representative industrial materials have been chosen. They are industrially important, and good student samples are relatively available. Many other common materials may be substituted, if samples are at hand.[3] The analytical methods given for these materials, although intentionally selected as given, are by no means the only ones available for some of the individual constituents concerned. Alternate procedures are suggested in the notes for some of the elements.

[1] Aluise *et al., Anal. Chem.* **19**, 347 (1947).

[2] See Chapter 32 for a list of such works.

[3] In order to use samples that will not vary in composition with time, recourse is often had to metallurgical and other inorganic substances of a stable nature. This fact explains the apparent emphasis on such samples in beginning courses in quantitative analysis. In general, however, the principles of analytical chemistry can be taught with any type of sample.

Exercise 31.1. Analysis of an Analytical Reagent Sodium Carbonate, Na_2CO_3

Wide variation in quality may be found between chemicals that are generally used and those required for particular purposes. Thus, technical-grade potassium dichromate serves for the preparation of "cleaning solutions." On the other hand, extreme care is necessary in the preparation and testing of potassium dichromate for use as a primary standard in redoximetry. This material, as N.B.S. Sample No. 136, is one of the most outstanding of all available analytical reagents.

In the examination of a new lot of reagent chemical, it is well to determine first that the material is actually that indicated on the label. Mislabeling can and does happen; if it occurs, the results of using such material might well range from nothing to dangerous reactions. Usually some simple test or determination, or a characteristic reaction, may be tried to settle the question. Further tests, such as those given below, will probably be necessary to determine the quality of the material.

Various compilations have been made of methods applicable to many common chemicals. As examples, Rosin's book[4] covers a wide range of reagents, and the United States Pharmacopoeia[5] contains specifications and tests for pharmaceutical products.

Of special concern to analysts are the specifications and test methods recommended by the Committee on Analytical Reagents of the American Chemical Society. These specifications are for reagents to be used in high-quality analyses. The limits and tests are based on published work, on the experience of members of the Committee in the examination of reagent chemicals on the market, and on studies and tests made by members of the Committee as the various items were considered. As an example of this important work, the material relating to sodium carbonate is reproduced herein.[6] References may be made to the book cited for methods for other substances.

Insofar as possible, the tests used in checking the purity of chemicals should be of the comparison, or "pass–no pass," types. That is, the test should be of such nature that, for specifications to be met a color or turbidity either should not appear within a given period of time, or should be less than that produced by a standard sample similarly treated. The requirements listed for sodium carbonate are the specifications for this compound if it is to be used in good analytical work.

[4] *Reagent Chemicals and Standards,* Van Nostrand, 1946.

[5] *Pharmacopoeia of the United States of America,* Mack Printing Company, 1950.

[6] Reproduced with permission of the Editor, Ed. Wichers, and of the American Chemical Society, from *Reagent Chemicals: American Chemical Society Specifications,* 1950.

Requirements

Insoluble matter. Not more than 0.010 per cent.
Loss on heating at 285°. Not more than 1.0 per cent.
Chloride (Cl). Not more than 0.005 per cent.
Nitrogen compounds (as N). Not more than 0.001 per cent.
Phosphate (PO_4). Not more than 0.001 per cent.
Sulfur compounds as SO_4. Not more than 0.004 per cent.
Ammonium hydroxide precipitate. Not more than 0.010 per cent.
Arsenic (As). Not more than 0.0003 per cent.
Calcium and magnesium precipitate. Not more than 0.015 per cent.
Heavy metals (as Pb). Not more than 0.0005 per cent.
Iron (Fe). Not more than 0.001 per cent.
Potassium (K). Not more than 0.02 per cent.

Tests (1)

Insoluble matter. Dissolve 10 g in 100 ml of hot water and allow to stand on the steam bath for 1 hour. Filter through a tared filtering crucible, wash thoroughly, and dry at 105°. The weight of the insoluble residue should not exceed 0.0010 g.

Loss on heating at 285°. Heat 1 g to constant weight at 270 to 300°. The loss in weight should not exceed 0.0100 g.

Chloride. Dissolve 1 g in water and 3 ml of nitric acid and dilute to 50 ml. To 10 ml of the solution add 1 ml of silver nitrate solution (0.1 *N*). Any turbidity should not exceed that produced by 0.01 mg of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Nitrogen compounds. Dissolve 1 g in 60 ml of water in a flask connected through a spray trap to a condenser, one end of which dips beneath the surface of 10 ml of 0.1 *N* hydrochloric acid. Add to the contents of the flask 20 ml of freshly boiled 10 per cent sodium hydroxide solution and 0.5 g of aluminum wire in small pieces. Allow to stand 1 hour and distill over about 35 ml. To the distillate add 1 ml of 10 per cent sodium hydroxide solution, dilute to 50 ml, and add 2 ml of Nessler reagent. The color developed should not exceed that produced when a quantity of an ammonium salt containing 0.01 mg of nitrogen (N) is treated exactly like the sample.

Phosphate. Dissolve 2 g in 10 ml of water, add 5 ml of hydrochloric acid, and evaporate to dryness on the steam bath. Take up the residue in 25 ml of approximately 0.5 *N* sulfuric acid, add 1 ml of ammonium molybdate solution (*2*) and 1 ml of *p*-methylaminophenol sulfate solu-

tion (*3*), and allow to stand for 2 hours at room temperature. Any blue color produced should not exceed that produced by 0.02 mg of phosphate (PO_4) in an equal volume of solution containing the quantities of reagents used in the test, including the residue from evaporation of 5 ml of hydrochloric acid.

Sulfur compounds. Dissolve 10 g in 100 ml of water, add 5 drops of bromine water, and boil. Cool, neutralize with hydrochloric acid, add an excess of 1 ml and filter. Boil the filtrate, add 5 ml of 10 per cent barium chloride solution, digest on the steam bath for 2 hours, and allow to stand overnight. Filter, wash thoroughly, and ignite. The weight of the ignited precipitate should not be more than 0.0010 g greater than the weight of the ignited precipitate from a complete blank test.

Ammonium hydroxide precipitate. Dissolve 10 g in 100 ml of water. Cautiously add 15 ml of sulfuric acid to 15 ml of water, cool, add the mixture to the solution of the sample, and evaporate to strong fuming. Cool, dissolve the residue in 130 ml of hot water, and add filtered ammonium hydroxide until the solution is just alkaline to methyl red. Wash with hot water, rejecting the washings, and ignite the precipitate. The weight of the ignited precipitate should not exceed 0.0010 g. The precipitate includes some, but not all, of the silica in the sample.

If a determination of the silica is desired, proceed as follows: Dissolve 10 g of the sample in 100 ml of water and acidify with sulfuric acid. Add 50 mg of iron (as ferric nitrate), dilute to 300 or 350 ml, make alkaline to litmus with ammonium hydroxide, boil for 2 minutes, filter, and wash with hot 2 per cent ammonium nitrate solution. Wash the precipitate off the paper into the original beaker, dissolve and reprecipitate. Filter again through the same paper, wash thoroughly, and ignite to 900°. Cool and weigh. Add 1 or 2 ml of hydrofluoric acid and 1 drop of sulfuric acid, evaporate, reignite at 900°, cool, and weigh. The loss in weight resulting from the treatment with hydrofluoric acid is due to silica (SiO_2). All operations must be done in platinum.

Arsenic. Dissolve 1 g in a small volume of water, neutralize with sulfuric or hydrochloric acid, and determine arsenic by the Gutzeit method. The stain produced should correspond to not more than 0.003 mg of arsenic (As).

Calcium and magnesium precipitate. Neutralize the filtrate from the test for *ammonium hydroxide precipitate* with hydrochloric acid and add an excess of 0.5 ml of the acid. Add 5 ml of 4 per cent ammonium oxalate solution, 2 ml of 10 per cent diammonium hydrogen phosphate solution, and 10 ml of ammonium hydroxide. Stir well and allow to stand

overnight. If any precipitate is formed, filter, wash with water containing 2.5 per cent of ammonia, and ignite. The weight of the ignited residue should not exceed 0.0015 g.

Heavy metals. To 5 g in a 150-ml beaker add 10 ml of water, mix, and add cautiously 10 ml of hydrochloric acid. For the control dissolve 1 g of the sample in 10 ml of water, add 0.02 mg of lead, and add cautiously 10 ml of hydrochloric acid. Evaporate both solutions to dryness on the steam bath, take up in 20 ml of water, add 1 drop of phenolphthalein indicator solution, and neutralize with 0.1 *N* sodium hydroxide. Add 1 ml of 1 *N* acetic acid to each, dilute to 40 ml, add 10 ml of hydrogen sulfide water, and mix. The color in the sample solution should not exceed that in the control.

Iron. Dissolve 1 g in 30 ml of water and 3.5 ml of hydrochloric acid. Dilute to 50 ml and add 30 to 50 mg of ammonium persulfate crystals and 3 ml of 30 per cent ammonium thiocyanate solution. Any red color should not exceed that produced by 0.01 mg of iron in an equal volume of solution containing 2 ml of hydrochloric acid and the quantities of ammonium persulfate and ammonium thiocyanate used in the test.

Potassium. Dissolve 1 g in 15 ml of water, add 3 ml of hydrochloric acid, evaporate to dryness on the steam bath, and heat for 30 minutes at 120°. Dissolve the salt in water to make a volume of 10 ml. To 5 ml of the solution add 5 ml of sodium cobaltinitrite solution (*4*) and slowly add 10 ml of alcohol with constant stirring. Any turbidity should not exceed that produced by 0.10 mg of potassium (K) in an equal volume of solution containing the quantities of reagents used in the test, including the residue from evaporation of 1.5 ml of hydrochloric acid.

NOTES: (1) Blank tests must be made on water and all reagents used in the tests unless the directions provide for the elimination of errors due to impurities. Solutions of samples must be filtered for tests in which insoluble matter would interfere.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified. "Water" means distilled water of a grade suitable for the test described. Reagents used in making the tests are supposed to be of a grade recommended by the Committee. A time of 5 minutes is to be allowed for the appearance of precipitates and before the observation of color reactions, unless some other time is specified.

(2) Dissolve 50 g of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$, in 1 liter of 1 *N* sulfuric acid.

(3) Dissolve 0.2 g of *p*-methylaminophenol sulfate, $(HOC_6H_4NHCH_3)_2 \cdot H_2SO_4$, and 20 g of sodium hydrogen sulfite, $NaHSO_3$, in 100 ml of water.

(4) Dissolve 25 g of sodium nitrite, $NaNO_2$, in 50 ml of water, add 5 ml of glacial acetic acid and 3 g of cobalt nitrate, $Co(NO_3)_2 \cdot 5\ H_2O$, dissolved in 15 ml of water, and dilute to 100 ml. This solution should be made up freshly for each set of tests.

Exercise 31.2. Partial Analysis of a Limestone Rock

The complete analysis of a rock consists in the determination of the constituents represented by the following formulas: **SiO_2**, TiO_2, ZrO_2, **Al_2O_3**, **Fe_2O_3**, Cr_2O_3, V_2O_3, $(CeY)_2O_3$, **FeO**, **MnO**, NiO, CoO, **MgO**, **CaO**, BaO, SrO, BeO, CuO, **Na_2O**, **K_2O**, Li_2O, **H_2O**, **CO_2**, **P_2O_5**, F, Cl, S, SO_3, and B_2O_3. The compounds in boldface are classified by Washington[7] as major constituents, and the other as minor constituents. For the present purpose we may simplify this list by (1) including TiO_2, Al_2O_3, Fe_2O_3, FeO, P_2O_5, and MnO under the general formula R_2O_3; (2) combining the H_2O (water of constitution) and CO_2, together with any organic matter that may be present, under the term "loss on ignition," and (3) omitting the determination of the alkalies, since their amount in limestone rocks is small. This leaves the following constituents to be determined: loss on ignition (roughly equalling CO_2), SiO_2, R_2O_3, CaO, and MgO. In contrast, the report for N.B.S. Standard Sample 1A, argillaceous limestone (high silica), lists 15 constituents.

The practice of reporting constituents as oxides is a reversion to the dualistic theory of Berzelius. According to this interpretation, a compound such as calcium carbonate may be considered as consisting of an acidic and a basic oxide; to indicate this, the formula could be written $CaO \cdot CO_2$. This practice has an analytical advantage in the present instance in that then the sum of the oxides should be 100 per cent. Although the method given herein does not provide for a number of the possible constituents noted above, the total of the five oxides to be determined often approximates 98 to 100 per cent of the sample.

Limestone rock is essentially calcium carbonate $CaCO_3$, contaminated with calcium silicate $CaSiO_3$, and with carbonates and/or silicates of one or more other elements. When magnesium (instead of calcium) is the major metal in such a rock, the rock is magnesite $MgCO_3$; dolomite, the intermediate stage, is a calcium magnesium carbonate.

The basis of the general procedure for the partial analysis of a carbonate rock is as follows: The loss on ignition is determined, using a platinum crucible and a Meker burner to attain a sufficiently high temperature. The residue is then solubilized by heating with sodium carbonate; this alkaline flux combines with the acidic silica, disrupting the silicates present in the sample. Following acidification, the silica, iron and aluminum, calcium, and magnesium can be separated in succession by precipitation, and converted into forms suitable for weighing. It may be noted that this all-gravimetric procedure uses a single sample for the five constituents or groups of constituents.

[7] *The Chemical Analysis of Rocks*, Wiley, 1930.

A successful analysis of a limestone rock can be accomplished only by careful attention to details. Before starting the analysis, the student should familiarize himself thoroughly with the procedure and with all precautions mentioned in the notes.

The Sample

Selection and preparation. The portions of rock selected for analysis should be ground to 100-mesh size and thoroughly mixed. Dry the sample in an oven at 105° for one-half hour.

Measurement. Weigh into a clean platinum crucible (*1*) a sample of 0.7 to 1.0 g (*2*). Both crucible and lid should be weighed.

NOTES: (1) The crucible should not only look clean but it should retain this appearance after heating at 900° for 15 minutes. If the heating produces a brownish appearance on the inside surface, contamination with iron is indicated. Directions for cleaning are given on page 475.

In the process of fusion of a rock containing more or less iron as FeO, sometimes the reaction

$$3\ FeO \rightarrow Fe_2O_3 + Fe$$

takes place and the iron alloys with the platinum of the crucible The alloy formed is not visible until strong heating forms a coating of the oxide, Fe_2O_3.

Platinum crucibles do not need to be heated to constant weight, as do most new porcelain crucibles. Before initial weighing, however, they should be heated to redness in a burner flame to remove any film of moisture

(2) Porcelain crucibles may be used if the residue is not to be ignited later with sodium carbonate. New crucibles should first be ignited to constant weight at the temperature to be used here.

The Desired Constituents

Loss on Ignition (CO_2)

The determination of loss on ignition of limestone differs experimentally from the procedure used for barium chloride dihydrate, chiefly in that it works at a much higher temperature. The conditions for thermal equilibrium for the $CaO \cdot CO_2$ system are discussed in texts on physical chemistry (see also Chapter 8).

Since loss on ignition is simply and quickly obtained, it is often taken as a rough measure of the content of carbon dioxide in the rock. Actually, the value obtained is the resultant of several possible reactions that may be partially compensating in their effect on the change in mass of the sample. Whatever is expelled at the temperature maintained (e.g., carbon dioxide, water vapor, and organic matter) produces a loss in weight, but oxidation of any ferrous iron or sulfide causes a gain.

Separation. Place the open crucible in an electric furnace (*1*) at 900 to 1000°. At the end of 45 min. remove the crucible and place it, with the cover on, in a desiccator.

Measurement. When the crucible is cool, weigh it (covered) (*2*). Repeat the heating and weighing until constant weight is reached. Calculate the percentage of loss on ignition (*3*).

NOTES: (1) A well-burning Meker-type burner may be used, but an electric muffle furnace is preferable.

In heating platinum crucibles with burners, care should be taken to keep the bottom of the crucible above the inner cone(s) of the flame. A reducing flame may cause the formation of brittle platinum carbide on the surface.

(2) The ignited residue, chiefly calcium oxide, readily absorbs carbon dioxide and water vapor from the air.

(3) The theoretical loss for pure calcium carbonate is 44 per cent. What may a higher value indicate?

Carbon Dioxide (CO_2)

If the simple determination of loss on ignition cannot be taken as a sufficiently reliable measure of the carbon dioxide, this constituent must be evolved, purified, and measured in some appropriate manner. The volatilization-gravimetric method, long used for this purpose, is described in Exercise 28.2, page 465.

Silica (SiO_2)

In order to solubilize high-silica limestone, the sample is ignited first with sodium carbonate. The hydrous silica resulting from the acidification of the solution must be dehydrated by double evaporation to render the silica insoluble and filterable. Since the residue so obtained is often contaminated, the impurities must be taken into account.

Separation. To the residue remaining in the platinum crucible from the determination of loss on ignition (*1*) add 1 g of sodium carbonate for each 10 per cent of silica, as estimated from the loss on ignition (*2*). Carefully mix it with the residue by means of a smooth-tip glass rod. Brush off any adhering particles with a small brush. Support the crucible on a chromel triangle and heat at low redness with a Meker-type burner for 5 to 10 min. Gradually raise the flame to full intensity and continue to heat for 30 min., keeping the crucible covered during the entire operation (*3*). If the silica is low, the mixture will form a sintered cake without becoming liquid. If the silica is high, the fused mass will appear as a viscous liquid, occasionally being clear.

Cool the crucible by placing it on a clean porcelain plate (*4*). After it has come to room temperature, place it in a 250-ml casserole, add 50 ml of water, and heat on a hot plate for 15 to 20 min.; this process serves to disintegrate the cake. Cover with a watch glass and add carefully 15 to 20 ml of concentrated hydrochloric acid. Heat for 5 to 10 min. on a hot plate and remove the crucible from the solution with a stirring rod, rinsing well with water. If the crucible is not clean, continue the treatment (*5*).

Cover the casserole with a watch glass supported on glass hooks, or with a ridged-surface watch glass. Evaporate the contents of the casserole to complete dryness on the hot plate (100°). Break any crust to determine that the residue is dry. Moisten with 5 ml of concentrated hydrochloric acid, add 50 ml of hot water, and heat on the hot plate until all the gritty particles of salt have dissolved. Filter through a No. 42 Whatman paper. Rinse the casserole with small volumes of dilute hydrochloric acid (1:20) and pour the rinsings through the filter paper. Thoroughly wash the paper and contents with 10 portions of hot hydrochloric acid (1:20) (*6*). Special care should be taken to wash the upper edge of the paper as well as the precipitate itself. Allow the paper to drain well between the addition of each portion of liquid.

Transfer the filtrate and washings to the original casserole and evaporate to dryness on the hot plate (100°) (*7*). Continue to heat for at least 1 hr. after dryness is reached (*8*). Moisten the residue with 2 to 3 ml of concentrated hydrochloric acid, add 25 ml of hot water, and heat gently until all gritty particles have dissolved. Filter through a new paper into a 400-ml beaker and wash with hot, dilute acid, as before. Small amounts of silica still adhering to the casserole may be wiped out with a small piece of moistened filter paper. This should be added to the contents of the funnel.

Transfer the two filter papers to a weighed platinum crucible, cover, and heat carefully with a Meker-type burner until dry (*9*). Continue the heating until the paper is black and all volatile matter is expelled. Push the lid to one side and heat the crucible more strongly, but not enough to bring the bottom of the crucible to more than a red color. The paper should not catch fire at any time and the burner flame should not completely envelop the crucible while carbon is still present. The intensity of heating can be controlled conveniently, first by supporting the crucible on a ring stand about 15 cm above the burner, and later gradually lowering it as the ignition proceeds. When all the paper has burned, ignite at a bright-red heat over a Meker-type burner for 30 min. Cool, weigh, and reignite to constant weight. Record the weight as Crucible +

$SiO_2 + R_2O_3$. The silica obtained in this way is usually contaminated with small amounts of R_2O_3.

Moisten the residue in the crucible with five to six drops of 25 per cent sulfuric acid (*10*) and then add about 5 ml of hydrofluoric acid (fill the crucible one-third full) (*11*). The latter and subsequent operation must be *carried out in a hood.* Place the crucible in an air bath (*12*) and heat until sulfur trioxide fumes cease to be evolved. Remove the crucible and ignite over a Meker-type burner for 15 min. at a bright-red heat (*13*). This operation removes the silicon as the tetrafluoride.

Measurement. When the crucible has been ignited to constant weight, weigh and record as Crucible + R_2O_3. The loss in weight represents the silica, and its percentage should be calculated.

The weight of any nonvolatile residue in the crucible should be added to the weight of R_2O_3 subsequently obtained.

NOTES: (1) A new portion of sample may be used here. If so, first oxidize any organic matter by heating the crucible containing the sample (without lid) to redness for 15 to 20 min. with a burner. Then proceed as directed under Separation.

(2) The percentage of "loss on ignition" provides a rough means of estimating the amount of silica, as shown in the following table:

Percentage Loss	*Percentage of Silica*
42 to 44	0.5 to 5
38 to 42	5 to 10
35	15 to 20
30	25 to 30
25	40 to 50

(3) Platinum crucibles may develop fine cracks after long use. Presence of such a crack, often not visually evident, is shown during this heating with sodium carbonate by the appearance of a strong sodium yellow in the burner flame at the location of the crack. A cracked crucible should be returned for repair following removal of the heated sample.

(4) A green color in the cool, fused mass indicates the presence of manganese, which often occurs in limestone to the extent of 0.1 to 0.2 per cent. In the analysis it distributes itself between the ammonia precipitate and the calcium and magnesium oxides. It may give the calcium oxide a light-brown color. It is usually neglected in ordinary industrial analyses.

(5) If a brownish stain of iron remains in the crucible, fuse with a small amount of potassium pyrosulfate, cool, and dissolve the melt in water. Precipitate with ammonia, as directed under the determination of iron and aluminum in the next section, filter, wash and ignite the paper, and combine the precipitate with that obtained in the main separation of iron and aluminum. This loss of iron is caused by reduction of iron compounds to metallic iron, which alloys with the platinum [see *Anal. Chem.* **26,** 591 (1954)].

(6) Dilute hydrochloric acid is used to wash the silica, to prevent contamination by basic salts of iron and aluminum which form as a result of hydrolysis if water alone is used.

(7) A double evaporation is necessary since not all of this constituent is rendered insoluble by the first evaporation.

(8) Prolonged heating of the residue at temperatures much above 100° causes part of the silica to form soluble compounds with magnesium and sodium, thus giving low results.

(9) Care must be used in burning filter paper. Too-rapid heating at least partially "fireproofs" the paper, making a white residue very difficult to obtain later. Start the burning with a Tirrill burner, and then finally ignite strongly with a Meker-type burner to remove the last traces of moisture. Keep the crucible in an upright position so that drafts will not carry out some of the finely divided material.

A dark residue may be treated once or twice with five drops of concentrated nitric acid, *carefully* heated (to avoid spattering), and again ignited. If a satisfactory residue cannot be obtained in this way, the material may contain some silicon carbide [see *Ind. Eng. Chem., Anal. Ed.* **8,** 118 (1936)]. In this case, start a new sample.

(10) Sulfuric acid is added along with hydrofluoric acid, to aid in the conversion of silica to the volatile fluoride by its dehydrating action:

$$SiO_2 + 6\ HF \rightarrow H_2SiF_6 + 2\ H_2O$$
$$H_2SiF_6 \rightarrow SiF_4\uparrow + 2\ HF\uparrow$$

After the excess hydrofluoric acid and the sulfuric acid are volatilized, the metallic constituents remain as the sulfates; see (*13*).

(11) Do not measure the hydrofluoric acid in a glass vessel. Bakelite ware is satisfactory.

(12) An air bath may be assembled with a No. 3 porcelain crucible and a piece of asbestos board (3 in. x 3 in.). Cut a hole in the center of the board slightly smaller than the diameter of the platinum crucible. Push the platinum crucible halfway through this hole and support the board on the rim of the porcelain crucible.

(13) Strong ignition of the residue from the silica is necessary to convert the sulfates into oxides.

Iron and Aluminum Oxides (R_2O_3)

The iron and aluminum in the silica filtrate are precipitated together with aqueous ammonia as the hydrous oxides. Dissolution and reprecipitation serve to purify the precipitate. Following ignition of the precipitate to the sesquioxides, $Fe_2O_3 + Al_2O_3$, they are weighed together and reported as such unless there is need to know each component.

Separation. To the filtrate from the silica (100 to 200 ml, in a 400-ml beaker) add 10 ml of concentrated hydrochloric acid and several drops of methyl red indicator (*1*). Heat the solution nearly to boiling and add filtered concentrated ammonium hydroxide until the solution is just alkaline (*2*). The presence of much iron may obscure the color of the indicator. In such cases the solution should be sufficiently alkaline to smell faintly of ammonia (*3*). Boil the solution gently two to three min. and

filter (*4*) as soon as the beaker can be handled (*5*), by decanting through a No. 42 Whatman paper and receiving the filtrate in a 600-ml beaker. Transfer the precipitate to the paper and rinse the beaker two or three times with 5-ml portions of a hot 2 per cent solution of ammonium chloride (*6*). Removal of the precipitate quantitatively from the beaker is not necessary. The rinsings should be poured over the filter. A second precipitation is necessary to purify the ammonia precipitate.

Remove the paper from the funnel, unfold, and spread out on the wall of the beaker in which the first precipitation was made in such a way that the upper edge of the paper is near the rim of the beaker. Wash the bulk of the precipitate into the beaker with a stream of hot water and dissolve it by the addition of a small amount of concentrated hydrochloric acid. During the dissolution of the precipitate the beaker may be tilted so that the solvent can act on the precipitate still adhering to the paper. When the precipitate has dissolved, dilute to 100 to 150 ml and reprecipitate with ammonium hydroxide, as described above. Disintegrate the filter paper from the first precipitation with the help of a stirring rod, and mix in with the precipitate.

Filter, while hot, on a new paper. Wash with eight to ten 5-ml portions of a hot 2 per cent solution of ammonium chloride, the washings being added to the filtrate. If difficulty is experienced in removing the last portion of precipitate, the surface of the beaker may be rubbed with a small piece of moistened filter paper which is then added to the precipitate. Acidify the filtrate (*7*) with hydrochloric acid and set aside for the determination of calcium and magnesium.

Transfer the precipitate and paper to a weighed porcelain (*8*) crucible. Heat carefully to remove moisture, and then gradually lower the crucible into the flame, taking care to carbonize and burn off the paper at a temperature as low as possible. When the paper is burned, tilt the crucible to one side, incline the lid in such a way as to admit air, and set the burner to bring the flame against the lower third of the crucible. The flame should not envelop the crucible. A Tirrill burner is more satisfactory than a burner of the Meker-type. Any reducing flame is likely to produce some of the lower oxide Fe_3O_4.

Measurement. After igniting until no further change takes place (*9*), weigh the residue. Add to the amount found the weight of the R_2O_3 residue obtained in the silica determination. Calculate the percentage of the R_2O_3 (*10*).

NOTES: (1) The addition of concentrated hydrochloric acid and subsequent neutralization with ammonium hydroxide insure the formation of sufficient ammonium chloride to prevent the precipitation of magnesium as $Mg(OH)_2$. In spite of this precaution,

some magnesium is carried down by adsorption and must be recovered by a second precipitation.

(2) Filtered ammonium hydroxide should be used as the precipitant to avoid adding the flakes of silica that usually contaminate the solution. Dropwise addition of strong acids and alkalies may be carried out conveniently by means of a medicine dropper. Do not use a pipet.

(3) An excess of ammonia may cause error through the formation of soluble aluminate.

(4) If there is a large precipitate of hydrous oxides, filtration may be expedited by adding a filtration "accelerator" or macerated pulp before filtering.

(5) Prolonged boiling or standing after the addition of ammonium hydroxide is to be avoided, since it tends to make the precipitate slimy and difficult to filter. In addition, carbon dioxide may be absorbed, causing part of the calcium to be precipitated as the carbonate.

(6) The ammonia precipitate is washed with a solution of ammonium chloride to prevent the passage of aluminum into the filtrate in colloidal form.

(7) Long contact of an alkaline solution with glass may dissolve some silica.

(8) If platinum crucibles are available, they are preferable at this point. In case any of the silica has not been caught in the preceding separation, it will accompany the R_2O_3 residue here. Treatment with hydrofluoric acid, as before, enables one to determine the amount lost. Any found here should be added to that found previously.

(9) When a large residue is obtained, completion of ignition is difficult to ascertain. In such cases, five to ten drops of concentrated nitric acid may be added. After careful volatilization, the residue is ignited again. Any partially reduced oxide will be reoxidized.

If there is much aluminum, the temperature of ignition should be 1000 to 1200° in order completely to dehydrate the Al_2O_3. An electric muffle furnace is most convenient.

(10) Iron may be determined separately by fusing the mixed oxides with potassium pyrosulfate, dissolving the mass in water, reducing the iron, and titrating with dichromate solution. Alternatively, the iron in the solution may be determined colorimetrically, as suggested in Exercise 29.4.

Calcium (CaO)

In the filtrate from the iron and aluminum the calcium is precipitated as the oxalate $CaC_2O_4 \cdot H_2O$. Dissolution and reprecipitation provide for elimination of the contamination by magnesium. The precipitate is usually ignited at 900° for the oxide CaO, for weighing. If the ignition is carried out at 500°, the residue will be the carbonate $CaCO_3$ (see page 117).

Separation. The volume of the filtrate may be 300 to 400 ml. Make the solution slightly ammoniacal to methyl red indicator, heat to boiling, and add slowly and with constant stirring 25 ml of a freshly prepared 4 per cent solution of ammonium oxalate. To insure an excess of pre-

cipitant, add 1 g of solid ammonium oxalate for each 100 ml of solution and then add 2 ml of concentrated ammonium hydroxide (*1*). Digest on the hot plate for 30 min., and then for at least 1.5 hrs. at room temperature (*2*).

Decant the filtrate through a No. 42 Whatman paper, but transfer as little as possible of the precipitate to the paper (*3*). Wash the main part of the precipitate in the beaker with two or three 10-ml portions of a cold 0.1 per cent solution of ammonium oxalate, and decant the washings through the filter between each portion. Place the beaker containing the main portion of the precipitate under the funnel and dissolve (*4*) the small amount on the paper by adding in small portions 50 ml of hot hydrochloric acid (1:4). Wash the paper thoroughly with hot water and discard the paper.

Heat the solution until all of the calcium oxalate has dissolved and dilute to 100 ml. Add 10 ml of a 4 per cent solution of ammonium oxalate, heat nearly to boiling, and reprecipitate by the dropwise addition of sufficient concentrated ammonium hydroxide to make the solution distinctly alkaline to methyl red. Digest on the hot plate as before and continue at room temperature for 4 to 6 hrs. or overnight.

Filter through a No. 42 Whatman paper and wash eight to ten times with small portions of a 0.1 per cent solution of ammonium oxalate. Unite the first and second filtrates with the washings, acidify with hydrochloric acid, and set aside for the determination of magnesium.

Transfer the precipitate and paper to a porcelain crucible (*5*) (weighed with lid) and heat slowly over a Tirrill burner to remove moisture. When the paper is dry, char and burn it, the same precautions being observed as with silica and iron and aluminum oxides. Transfer the crucible to a muffle furnace and ignite uncovered at 1000° for 30 min.

Measurement. Weigh with the lid (*6*) as soon as cool and reignite to constant weight. Calculate the percentage of calcium oxide.

NOTES: (1) Some prefer to use urea to make the solution alkaline (see page 427).

(2) If much magnesium is present, the precipitate should not be left too long in contact with the solution on account of the possibility of extensive contamination with magnesium oxalate through postprecipitation.

(3) The main part of the precipitate of calcium oxalate from the first precipitation should not be transferred to the filter, as the salt is not easily redissolved in the acid.

(4) The first precipitate of calcium oxalate invariably contains some magnesium and sodium, and hence must be dissolved and reprecipitated.

(5) If titrimetric measurement of the calcium is preferred, proceed at this point as directed on page 426.

(6) Since calcium oxide takes up moisture and carbon dioxide from the air, weighing should be made as rapidly as possible. After the approximate weight has been

obtained, the time for remaining weighings may be reduced by placing the weights on the balance pan before the crucible is removed from the desiccator. The final adjustment must be made with the rider (or chain).

Magnesium (MgO)

Magnesium in the calcium filtrate is precipitated as the phosphate $MgNH_4PO_4 \cdot 6\ H_2O$. Here dissolution and reprecipitation provide both for the elimination of contamination and for obtaining the desired composition of the precipitate. Ignition at 1000° yields the pyrophosphate $Mg_2P_2O_7$.

Separation. Make the combined filtrates, which may have a volume of 400 to 500 ml, slightly acidic to methyl red with hydrochloric acid. Add enough diammonium hydrogen phosphate, as a filtered 10 per cent solution or as a solid, to provide at least a tenfold excess of phosphate. In addition, add 1 g for each 100 ml of solution. Stir the solution vigorously and basify by the dropwise addition of concentrated ammonium hydroxide (*1*). When the solution is just alkaline, add an excess of 10 ml, also dropwise, for each 100 ml of solution. Digest at room temperature (*2*) overnight (preferably for 20 hrs.) (*3*). If the amount of magnesium is small, precipitation may be hastened by cooling to 10°.

Decant the solution through a No. 42 Whatman paper, transferring to the filter as little as possible of the precipitate. Wash the precipitate in the beaker twice with cold ammonium hydroxide (1:10), the washings being decanted through the filter (*4*). Dissolve the precipitate by pouring 25 ml of warm hydrochloric acid (1:4) through the filter, the solution being received in the beaker in which the first precipitation was made. Wash the paper with hot water, and discard.

Dilute the filtrate to 50 to 150 ml, the volume depending upon the amount of magnesium present. Add 0.3 g of diammonium hydrogen phosphate and basify to methyl red by the dropwise addition of concentrated ammonium hydroxide, accompanied by constant stirring. When a slight excess has been obtained, add 5 ml more for each 100 ml of solution. Digest for at least 4 hrs., or, preferably, overnight. Filter into a Gooch crucible, ignited in a muffle furnace at 1000°. Wash 3 to 4 times with ammonium hydroxide (1:10). Dry the precipitate in an oven at 110° and then ignite to constant weight in the muffle furnace at 1000° (*5, 6*).

Measurement. Weigh the residue of magnesium pyrophosphate $Mg_2P_2O_7$, and calculate the percentage of magnesium oxide.

NOTES: (1) The chemistry involved in this precipitation is more complicated than any encountered thus far. At this stage of the analysis at least the following ions must be assumed to be present: H^+, NH_4^+, Na^+, Mg^{+2}, OH^-, Cl^-, $C_2O_4^{-2}$, and PO_4^{-3}. Much experimentation has shown that the preferable inorganic form for separating the magnesium is magnesium ammonium phosphate $MgNH_4PO_4 \cdot 6\ H_2O$, and that the conditions prescribed in the procedure will yield this compound. For interpretations of the various details, reference should be made to more extensive works.

(2) Since magnesium ammonium phosphate may be slow to precipitate, the solution should stand overnight before filtering. Even then, because of possible supersaturation of the solution, the lack of appearance of a precipitate cannot be assumed as indicative of the absence of magnesium. In such a case, try to induce crystallization by rubbing with a glass stirring rod the inside surface of the beaker below the surface of the solution. If no precipitate then appears, the solution probably does not contain enough magnesium to produce a precipitate.

(3) Digestion at this temperature is necessary both to keep the solubility of the precipitate down and to prevent undue loss of ammonia from the solution.

(4) Washing with water, or with too-dilute ammonium hydroxide, may give a turbid filtrate containing colloidally dispersed magnesium hydrogen phosphate, produced according to the equation

$$MgNH_4PO_4 + H_2O \rightarrow MgHPO_4 + NH_4OH$$

(5) Some analysts prefer to wash the precipitate finally with ethanol and then diethyl ether. The magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6\ H_2O$, is dried 15 min. at room temperature in the open air and weighed as such. Obviously, meticulous care must be taken to retain the six molecules of water.

(6) 8-Hydroxyquinoline has some devotees as a precipitant for magnesium. Although weighing the precipitate $Mg(C_9H_6ON)_2 \cdot 2\ H_2O$ as such, has been proposed, there is doubt regarding the composition after drying. Two alternatives for handling it are available: (1) the compound may be ignited, with ultimate conversion to magnesium oxide, MgO, or weighing; and (2) the magnesium in the compound may be determined indirectly by means of a series of titrimetric reactions that involve bromination of the quinoline ring in the 5, 7 positions. The following equations apply in the latter case:

Precipitation:

$$Mg^{+2} + 2\ HOC_9H_6N + 2\ OH^- \rightarrow Mg(C_9H_6ON)_2 \cdot 2\ H_2O \downarrow$$

Dissolution in acid:

$$Mg(C_9H_6ON)_2 \cdot 2\ H_2O + 2\ H^+ \rightarrow Mg^{+2} + 2\ HOC_9H_6N$$

Bromination (in excess):

$$BrO_3^- + 5\ Br^- + 6\ H^+ \rightarrow 3\ Br_2 + 3\ H_2O$$
$$HOC_9H_6N + 2\ Br_2 \rightarrow HOC_9H_4NBr_2 + 2\ HBr$$

Back titration:

$$Br_2 + 3\ I^- \rightarrow (I_2)I^- + 2\ Br^-$$
$$(I_2)I^- + 2\ S_2O_3^{-2} \rightarrow 3\ I^- + S_4O_6^{-2}$$

Exercise 31.3. Analysis of Brass

The alloy known for many centuries as "brass" may contain only two elements, copper and zinc, which give the familiar yellow brass when the amount of zinc is fairly large. In modern metallurgical practice, however, it has become fairly common to make brass containing four or more elements. Similarly, the term "bronze" once referred to copper-tin alloys, but in this case also, such simple alloys are becoming increasingly uncommon. For the present purpose, the analysis of brass and bronze is considered as one topic.

Considering such alloys together, then, one may expect to find in almost any common brass or bronze at least a small amount of each of the following elements: copper, iron, lead, tin, and zinc. In addition, a small amount of nickel is commonly found as an essential constituent.

Lists of alloys include hundreds of different brasses and bronzes.[8] The maximum number of deliberately added elements in any one of these alloys is not likely to exceed seven. In addition to the six metals already mentioned, the following elements are fairly common: aluminum, antimony, arsenic, manganese, phosphorus, silicon, and vanadium. Other elements that are sometimes present in special or experimental alloys are the following: beryllium, bismuth, cadmium, calcium, cerium, chromium, gold, magnesium, selenium, silver, sulfur, tellurium, titanium, and zirconium.

For the analysis of such alloys various methods, with many variations in details, have been proposed. Some analysts employ only one kind of measurement throughout; other analysts prefer several. To illustrate the variety of methods used by nine co-operating laboratories, the N.B.S. report for the analysis of a sheet brass is given in Table 31.1. The names of the analysts and their laboratories are omitted. Incidentally, the results listed in Table 31.1 indicate the degree of concordance attainable by different competent analysts, using reliable methods, on a homogeneous sample.

Two methods of analysis are included in this discussion. The first procedure is designed for gravimetric measurement of all six constituents of brass (Cu, Fe, Ni, Pb, Sn, Zn), with the directions for analysis written in the general form adopted for this book. Thus, the separate steps of separation and measurement are emphasized, and explanatory notes are given for many details.

In contrast, the second procedure is that employed by the American Society for Testing Materials for the use of industrial analysts. By

[8] See Wilkins and Bunn, *Copper and Copper-Base Alloys*, McGraw-Hill, 1943.

TABLE 31.1

ANALYSIS OF N.B.S. STANDARD SAMPLE 37D, SHEET BRASS
(in per cent)

Analyst	*Cu*	*Zn*	*Sn*	*Pb*	*Ni*	*Fe*
	Electrolytic	ZnS-ZnO	$SnCl_2$-Iodine	Electrolytic	Weighed as Nickel Dimethyl-glyoxime	
1	70.78[a]	26.65	0.96[b]	0.94	0.57	0.074[c]
2	70.77[d]	26.62	0.97[e]	0.94	0.58	0.077[f]
3	70.77[g]	26.65	0.96[h]	0.94[g]	0.57	0.081[i]
4	70.79[j]	26.64	0.97[k]	0.94	0.58	0.074[l]
5	70.78[a]	26.66	0.97[m]	0.93	0.57	0.081[n]
6	70.79[g]	26.65	0.96[m]	0.95	0.57[o]	0.08[p]
7	70.76[q]	26.66	0.97[r]	0.93[s]	0.58	0.07[t]
8	70.78	26.66	0.97[m]	0.94	0.58	0.074[n]
9	70.77[a]	26.65	0.97[u]	0.95	0.58[v]	0.077[w]
AV.	70.78	26.65	0.97	0.94	0.58	0.076

[a] Five-gram sample dissolved in 100 ml of HNO_3 (1:4). Solution digested overnight on a steam bath, filtered, and the precipitate washed with hot HNO_3 (1.99). Filtrate diluted to 350 ml, two drops of 0.1 *N* HCl added, and solution electrolyzed overnight by the use of a current density of 0.5 amp./dm^2. Metastannic acid precipitate and paper treated with HNO_3-H_2SO_4. Tin, antimony, and arsenic volatilized by HBr-Br_2, and the residual solution combined with the electrolyte. Residual copper and lead in the combined solutions precipitated with H_2S and determined by electrolysis.

[b] Five-gram sample dissolved in HNO_3 (1:2). An excess of NH_4OH added. Precipitate separated and digested with HNO_3-H_2SO_4. Tin distilled with HBr-HCl, precipitated with cupferron, and ignited to SnO_2 [see *J. Research Nat. Bur. Standards* **33**, 307 (1944)].

[c] Filtrate from the copper sulfide precipitation (footnote *a*) boiled to remove H_2S. Iron oxidized and precipitated twice with NH_4OH. Precipitate dissolved and iron determined by the $SnCl_2$-$K_2Cr_2O_7$ method.

[d] Two-gram sample dissolved in HNO_3-H_2SO_4; lead sulfate filtered off, and filtrate electrolyzed for copper in the presence of tin.

[e] Tin reduced with aluminum.

[f] Five-gram sample treated with HNO_3. Metastannic acid precipitate separated, tin volatilized by treatment with $HClO_4$-HBr. Residual solution added to main solution. Iron precipitated with NH_4OH. Precipitate dissolved, and iron determined by the $SnCl_2$-$K_2Cr_2O_7$ method.

[g] Copper and lead deposited in an HNO_3-HF solution in the presence of tin. PbO_2 replated in HNO_3 (1:13).

[h] Tin reduced with iron coil in the presence of added antimony.

[i] Iron reduced with zinc and titrated with $KMnO_4$.

[j] As in (d), except a 5-g sample used.

[k] Tin reduced with nickel and titrated with KIO_3.

[l] $FeCl_3$-photometric method.

[m] Tin reduced with test lead.

[n] Iron reduced with $SnCl_2$ and titrated with $K_2Cr_2O_7$.

[o] Potassium dithiooxalate-photometric method.

[p] Iron reduced with H_2S and titrated with $Ce(NH_4)_4(SO_4)_4$ using ferrous-1,10-phenanthroline indicator.

[q] As in (a), except copper, lead, and iron in the metastannic acid precipitate recovered by the alkaline-sodium sulfide method.

[r] Tin reduced with test lead in the presence of added antimony.

[s] Weighed as $PbCrO_4$.

[t] Weighed as Fe_2O_3.

[u] Tin reduced with iron and titrated with KIO_3.

[v] Dimethylglyoxime-photometric method.

[w] NH_4SCN-photometric method.

working from those directions the student may become somewhat familiar with the kind of writing he is likely to encounter in practical work. Such methods are usually written in the imperative, "cookbook" style, with little or no explanatory material given concerning the principles involved or the details specified.[9]

Method I. All-Gravimetric Procedures

This procedure is based on the successive separation of six metals from a single sample, and the gravimetric determination of each one. The electrodeposition of copper is the only separation not made by precipitating an insoluble compound of the desired metal.

The Sample

Selection. From the material at hand, secure drillings or millings that are clean (*1*) and representative of the stock metal.

Measurement. Weigh accurately about 2 g of the sample and transfer to a 250-ml casserole. Cover with a glass.

NOTE: (1) If the sample carries oil from a drill or other cutting tool, the material should be washed with a solvent, such as diethyl ether. It is well also to pass a magnet over the sample material to remove any adventitious iron particles.

The Desired Constituent

Tin separation. Lift the cover glass somewhat and add 25 ml of nitric acid (1:1). When rapid action ceases (*1*), digest for 3 hrs. at a temperature near the boiling point of the solution (*2*). With a stirring rod, crush any large particles not dissolved. If an appreciable amount of tin is present (*3*), it will appear here as the insoluble, white hydrous oxide (*4*). Add 50 ml of water, together with a paper filtration accelerator (*5*) and filter through a No. 42 Whatman paper (*6*). Catch the filtrate in a casserole. After transferring the precipitate and added paper to the filter, wash thoroughly with hot water (*7*). Set the filtrate aside for the determination of lead.

In burning the paper, use a porcelain crucible supported in a sheet of asbestos, and heat slowly with a Tirrill burner until charring and combustion are complete. Allow free access of air at all times (*8*). Cool the crucible, moisten the residue with two or three drops of concentrated nitric acid, and volatilize the excess acid carefully. Finally, ignite the residue at the full temperature of the Tirrill burner, cool and weigh (*9*).

[9] Similarly written, official methods are those of the American Public Health Association (A.P.H.A. methods), the Association of Official Agricultural Chemists (A.O.A.C. methods), and the American Pharmaceutical Association (U.S.P. methods).

If the residue is dark (*10*), indicating coprecipitation of lead, copper, and iron, add to the impure stannic oxide about 15 times its weight of finely powdered ammonium iodide (*11*) and mix the two intimately in the crucible by means of a small spatula (*12*). Place the charged crucible in an electric furnace maintained between 425 and 475°. Allow the crucible to remain until all fumes cease coming from the crucible, which should require about 15 min. Remove the crucible, allow it to cool nearly to room temperature, and add 2 to 3 ml of concentrated nitric acid. Evaporate to dryness on the hot plate and cautiously decompose the residual nitrates over a low burner flame. Then ignite at a dull-red heat to constant weight.

Measurement. Weigh the final residue. The difference between this value and that obtained for the unpurified residue gives the weight of the stannic oxide. Calculate the percentage of tin.

Any material remaining in the crucible following the ammonium iodide treatment may contain copper, iron, and lead. To dissolve such a residue add a few ml of hot concentrated hydrochloric acid. Dilute the resulting solution and filter to remove small amounts of silica that may come from the filter ash. Add the filtrate and washings to the filtrate that is to be evaporated for the determination of lead.

NOTES: (1) The heavy brown fumes evolved are poisonous. Keep the casserole in the hood.

(2) Some analysts prefer to evaporate the solution to dryness on a steam bath and then dissolve the soluble salts in 1 *M* nitric acid.

(3) Unless the solution is entirely clear, it should be filtered and tin assumed to be present. Use of a black-glaze casserole helps the analyst to see any fine particles.

(4) Often the insoluble substance is called metastannic acid, although there is evidence that it is really a hydrous oxide for which the formula $SnO_2 \cdot xH_2O$ may be written.

(5) Compressed tablets of filter paper form the "accelerator." Put one in a test tube, along with 10 ml of water, shake vigorously, and add the suspension to the system to be filtered. An ordinary filter paper, torn into fine pieces, will serve.

(6) If much tin is present, use of a suction flask for filtering may be advantageous. If so, use a platinum or tantalum cone in the apex of the funnel to support the paper.

(7) Cupric salts are completely removed only by prolonged washing. A dried filter paper at this point often shows a blue ring around the top unless the washing is done thoroughly.

(8) Stannic oxide is very easily reduced to metallic tin if the oxygen supply in the crucible is inadequate. A platinum crucible, by alloying with the metallic tin, may easily be ruined in this operation.

(9) The residue is always contaminated somewhat, the entrainees being any phosphorus and some copper, iron, and lead. If the residue is small (as with low-tin samples) and yellowish-white in appearance, its purification may be omitted for routine work. Extensive entrainment of copper may yield a nearly black residue.

(10) The method given here of correcting for entrained matter is only one possibility. For alloys high in tin a better approach is to follow the procedure given in the ASTM methods described in Method II. In this case, the tin is determined titrimetrically.

(11) If the ammonium iodide leaves a nonvolatile residue on volatilization, the percentage of nonvolatile matter must be determined and a correction applied. This means also that one must use a known amount for each treatment.

(12) A great difficulty here is to get two solids hot enough to react, without at the same time decomposing the ammonium iodide ($NH_4I \rightleftarrows NH_3\uparrow + HI\uparrow$).

Lead separation.[10] To the entire filtrate from the tin determination, contained in a casserole, add 5 ml of concentrated sulfuric acid and evaporate (*1*) to dense, white fumes of sulfur trioxide (*2, 3*). Allow the solution to cool, add 35 ml of water, boil for 1 min. to dissolve soluble salts, and allow to stand 1 hr. Transfer the cool solution and the precipitate by means of a stream of sulfuric acid (1:20) to a weighed Gooch crucible. Use a clean filter flask for the filtrate. Wash with the dilute acid. After completion of the washing with dilute acid, transfer the filtrate to a 250-ml volumetric flask. Ignite the crucible at 600° in an air bath to constant weight.

Measurement. Weigh the residue of lead sulfate $PbSO_4$, and calculate the percentage of lead.

NOTES: (1) This evaporation may be troublesome if there is enough lead sulfate to cause "bumping" when the solution becomes concentrated. Allowing the casserole to sit over a flame is hazardous, since one "bump" may ruin the determination.

If time is available, set the casserole on a steam hot plate, raise the cover glass on hooks, and allow the water to evaporate. Then remove the glass and support an infrared lamp about 5 mm above the rim of the casserole until the sulfuric acid begins to fume. A more rapid, but tiresome procedure consists in holding the casserole over a low flame, maintaining *continuous* agitation by swirling the contents of the vessel.

(2) The nitric acid must be entirely volatilized to render the lead sulfate sufficiently insoluble.

(3) During or preceding the evaporation, a Gooch crucible should be prepared, the

[10] A simultaneous electrodeposition of lead and copper from the nitric acid solution is sometimes recommended, especially for alloys low in lead (see ASTM method in Method II). Lead deposits on the anode as the dioxide, and copper on the cathode as the metal. Two difficulties may be encountered. For complete deposition of the lead, the solution should contain 10 to 15 per cent of nitric acid, an acidity that makes complete deposition of copper difficult. Also, if much lead is present, it does not adhere well to the electrode after drying. The deposit may be improved somewhat by adding a few drops of hydrogen peroxide to the solution being electrolyzed. A platinum dish may be used as the anode and the solution siphoned out on completion of the deposition.

If the amount of lead is small, electrolyze the solution, containing at least 10 per cent of nitric acid, for lead. Make the spiral electrode the anode. When deposition of the lead is complete, remove the anode, dry at 120° for 30 min., weigh the dioxide, and calculate the percentage of lead. Put in another anode, nearly neutralize the excess acid with filtered ammonium hydroxide, and continue the deposition of the copper.

mat being washed with dilute sulfuric acid. Ignite in an air bath at about 600° (see Note *12* in the material on determination of silica in limestone, page 570).

Copper separation. Dilute to the mark on the volumetric flask the filtrate from the lead determination. Transfer a 50-ml aliquot to a 200-ml tall-form beaker (*1*), and add filtered concentrated ammonium hydroxide until a precipitate of cupric hydroxide just appears. Then add 2 ml of concentrated nitric acid to dissolve any precipitate, and mix the solution.

Separate the copper by electrodeposition according to the directions given on page 491, 0.5 g of urea being added when the color of the cupric ion is almost gone (*2*). In order to prevent the possibility of depositing zinc, keep the voltage below 2.5 (*3*). When the deposition of copper is complete, set aside the solution in the beaker for subsequent determinations (*4*).

Measurement. Weigh the cathode with the deposit of copper. Dissolve the copper by heating in hot, dilute nitric acid. Rinse the electrode in water, dry, and reweigh. The difference in weight is the copper deposited. Calculate the percentage of copper.

NOTES: (1) A tall, lipless form of beaker is preferable for electrolytic work.

(2) Urea reacts with any nitrite ion produced at the anode by reduction of the nitrate ion.

(3) A rotating anode permits a much higher rate of deposition without giving unsatisfactory deposits.

(4) A brownish or black deposit on the anode is probably a little lead. If such a deposit appears, dry the electrode and handle as directed in footnote 10, page 580. To dissolve the lead dioxide, heat with dilute nitric acid, containing a reductant, such as oxalic acid.

Iron (and aluminum) separation. Transfer the solution from which the copper was deposited to a 250-ml ordinary beaker, add a few drops of hydrogen peroxide (*1*), and boil gently for a few minutes, to destroy excess peroxide (*2*). Add two drops of methyl orange indicator, basify with filtered ammonium hydroxide, and then add 5 to 10 ml excess. If the sample is yellow brass, 1 to 2 g of ammonium chloride should be added before the ammonium hydroxide, to keep the zinc from precipitating. If a heavy precipitate, which is obviously zinc hydroxide, appears, dissolve in sulfuric acid and reprecipitate. If no visible precipitate appears on boiling the solution gently, proceed with the determination of zinc. It may then be assumed that no iron (or aluminum) is present.

If there is a precipitate of hydrous ferric oxide (and/or hydrous aluminum oxide), boil out the excess ammonium hydroxide, filter on paper, and wash with 2 per cent ammonium nitrate solution. Proceed with

the precipitate as directed for the ammonia precipitate in the analysis of limestone (page 570) (*3, 4*). Reserve the filtrate for the determination of zinc. Calculate the percentage of iron (or aluminum) (*5*).

NOTES: (1) Hydrogen peroxide will oxidize any reduced iron.

(2) Strong oxidants may destroy the color of methyl orange indicator.

(3) If there is only a small hydrous oxide precipitate, dissolution and reprecipitation may be omitted.

(4) If both oxides are present, after weighing they may be fused with potassium pyrosulfate, dissolved in water, and the iron reduced and titrated. Or the iron may be determined colorimetrically (see page 510).

(5) If the residue is brown, assume it is iron oxide Fe_2O_3; if it is not brown, assume it is aluminum oxide Al_2O_3.

Zinc separation. To the filtrate from the iron determination add another drop of methyl orange indicator, and then add just enough 10 per cent hydrochloric acid to turn the solution pink. To the hot solution add dropwise 25 ml of a 10 per cent solution of diammonium hydrogen phosphate (*1*), and digest the precipitate on the steam hot plate for 45 min. The *p*H should be 6 to 6.5 (*2*), as shown by nitrazine test paper (*3*). Cool somewhat, and filter on a Gooch crucible. Wash the precipitate first with a 1 per cent solution of the precipitant until it is free of sulfate (*4*) and, finally, with three 5-ml portions of 50 per cent ethanol. Ignite the precipitate to constant weight at 900° (*5*).

Measurement. Weigh the residue, $Zn_2P_2O_7$, and calculate the percentage of zinc.

NOTES: (1) Dissolve the diammonium hydrogen phosphate $(NH_4)_2HPO_4$, in water and then add ammonium hydroxide until the solution is just alkaline to phenolphthalein. If not clear, filter before use.

(2) Below *p*H 5 the precipitation is incomplete, because of partial conversion of secondary to primary phosphate

$$HPO_4^{-2} + H^+ \rightleftarrows H_2PO_4^-$$

Above *p*H 7.7 incomplete precipitation results from the formation of a complex ion

$$Zn^{+2} + 4\ NH_3 \rightleftarrows Zn(NH_3)_4^{+2}$$

(3) At the respective *p*H values, nitrazine paper shows the hues indicated: 4.5, yellow; 5.0, mustard-yellow; 5.5, olive-yellow; 6.0, olive-green; 6.5, dark-green; 7.0, gray-blue; 7.5, deep-blue.

(4) Acidify the solution with hydrochloric acid before testing for sulfates.

(5) Some analysts prefer to dry the precipitate at 105° and weigh the residue as zinc ammonium phosphate $ZnNH_4PO_4$.

Nickel separation. To the filtrate from the zinc determination add 2 to 5 ml of filtered, concentrated ammonium hydroxide and 10 ml of 1 per cent dimethylglyoxime (in 95 per cent ethanol) (*1*). Then proceed

with the precipitate of dimethylglyoxime as directed for the determination of nickel in steel, page 486. Calculate the percentage of nickel (*2*).

NOTES: (1) See the notes for the determination of nickel in steel regarding the importance of adding approximately the needed amount of precipitant.

(2) Many analysts now prefer the colorimetric method for determination of nickel, especially for small amounts.

Method II. Standard Methods for Chemical Analysis of Special Brasses and Bronzes[11]

ASTM Designation: E 54-49
Adopted, 1949

This Standard of the American Society for Testing Materials is issued under the fixed designation E 54; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

This procedure follows the ASTM recommendations[12] for special brasses and bronzes. Thus, provision is made for certain elements, and certain ranges of elements, not covered in the previous procedure. It will be noted that several different samples are used, rather than only just one. Also, this procedure contains a number of differences in methods used for the individual elements. These differences illustrate the varied preferences of analysts in dealing with such problems.

Limitations of space preclude giving the entire procedure. However, note is made of the items omitted, in case some particular sample requires a method not included.

NOTE TO THE STUDENT: For applying the ASTM methods (given hereafter) to copper-base alloys, a series of successive steps for organizing the work is suggested below. The numbers and letters given in parentheses in these suggestions refer to individual sections in the ASTM procedure that are similarly designated.

1. Weigh and dissolve the sample (Section 6*a*).
2. Determine copper and lead simultaneously by the electrolytic method of separation (Section 6*d*). Save the solution and washings from the electrodeposition process.
3. Dilute the solution from Section 6*d* to 250 ml in a volumetric flask. Use aliquots of this solution, as noted here.
4. In the first 50-ml aliquot, determine zinc by precipitation as the sulfide and by ignition to the oxide (Sections 16*c* through 16*h*).
5. In the second 50-ml aliquot determine nickel by precipitation as the dimethylglyoxime complex (Section 25).
6. In the third 50-ml aliquot, determine the iron and aluminum oxides together

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(Sections 22*i* to 22*m*). The iron in the precipitate may be determined separately (Section 26).

7. On a separate sample, determine tin titrimetrically (Section 12).

Scope

1. (*a*) These methods cover procedures for the chemical analysis of the commercial alloys known as copper-base alloy ingots for sand castings, forging rods, bars, and shapes; aluminum brass; manganese bronze; phosphor bronze; copper-silicon alloys; and similar alloys having chemical compositions within the following limits:[13]

	Range (per cent)
Copper	50 and over
Lead	0.0 to 27
Tin	0.0 to 20
Silicon	0.0 to 5
Aluminum	0.0 to 12
Nickel	0.0 to 5
Iron	0.0 to 5
Manganese	0.0 to 6
Sulfur	0.0 to 0.1
Phosphorus	0.0 to 1.0
Arsenic	0.0 to 1.0
Antimony	0.0 to 1.0
Zinc*	0.0 to 50

* In the case of copper-base alloys containing 5.0 per cent and over of zinc, the zinc is usually calculated by difference.

Whenever possible the technics and procedures for analysis should be checked against a National Bureau of Standards standard sample having a composition comparable to the material being analyzed.

Apparatus and Reagents

2. Apparatus and reagents required for each determination are listed in separate sections preceding the procedure. The apparatus, standard solutions and certain other reagents used in more than one procedure are referred to by number and shall conform to the requirements prescribed in the Tentative Recommended Practices for Apparatus and Reagents for Chemical Analysis of Metals (ASTM Designation E 50).[14]

[13] For procedures for the chemical analysis of other brasses, see the Standard Methods for Chemical Analysis of Brasses (ASTM Designation: E 36), *1950 Book of ASTM Methods for Chemical Analysis of Metals,* p. 249. For photometric procedures applicable to special brasses and bronzes, see the Tentative Photometric Methods for Chemical Analysis of Copper and Copper-Base Alloys (ASTM Designation E 62), *1950 Book of ASTM Methods for Chemical Analysis of Metals,* p. 290.

[14] *1950 Book of ASTM Methods for Chemical Analysis of Metals,* p. 1.

Precautions

3. For precautions to be observed in these methods, reference shall be made to ASTM Recommended Practices E 50.

Copper, or Copper and Lead Simultaneously, by Electrodeposition as Copper and as Lead Dioxide

Apparatus

4. (*a*) *Electrodes for Electroanalysis.* Either stationary or rotating type.

(*b*) *Gooch Crucible.* Usual type, heated at 600°C.

Reagents

5. (*a*) *Sodium Sulfide Solution (250 g per l).*

(*b*) *Sodium Sulfide Solution (20 g per l).*

(*c*) *"Lead Acid" Solution.* Add 150 ml of H_2SO_4 to 900 ml of water. Dissolve 0.5 g of lead acetate in 150 ml of water and add to the hot H_2SO_4 solution while stirring. Allow the solution to stand for at least 24 hr. and siphon or decant through a thick asbestos filter.

(*d*) *Lead Nitrate Solution (10 g per l).*

Procedure for Alloys Containing 1.5 per cent and Over of Tin, Under 6.0 per cent of Lead, and Under 0.5 per cent of Silicon.[15]

6. (*a*) Transfer 2.000 g of the sample to a 250-ml beaker, cover, and decompose with 25 ml of HNO_3 (1:1). Heat on a steam bath and boil gently to expel brown fumes. Add 50 ml of hot water, and allow to stand on a steam bath for 1 hr. Add paper pulp and filter off the metastannic acid through a close-texture paper into a 250-ml beaker. Wash several times with hot HNO_3 (1:99), and reserve the filtrate and washings. Continue the determination as described in Paragraph (*b*) or (*c*).

(*b*) Transfer the filter paper and contents to the original beaker, and add 15 ml of H_2SO_4 and 25 ml of HNO_3. Heat until all organic matter is decomposed. Transfer the digested solution to a 400-ml beaker, and dilute to 250 ml. Add NaOH (250 g per l) until the solution is alkaline

[15] If more than 6.0 per cent of lead is present, the copper only shall be determined by this procedure as the lead deposit is not sufficiently adherent to the anode for safe handling. The lead shall then be determined on a separate sample as described in Sections 10 and 11. If the expected tin content is under 1.5 per cent, the analysis may be more conveniently carried out in accordance with the procedure described in Sections 7, 8, and 10 of the Standard Methods of Chemical Analysis of Brasses (ASTM Designation: E 36), *1950 Book of ASTM Methods for Chemical Analysis of Metals,* p. 251. For copper-silicon alloys the procedure described in Section 7 should be used.

and the tin hydroxide has dissolved. Add 20 ml of Na_2S (250 g per 1), stir thoroughly, and digest on the steam bath for several hours, or until the supernatant liquor is clear. Cool to room temperature, filter through a close-texture paper, and wash the precipitate with Na_2S (20 g per 1). Dissolve the residue in a few milliliters of HNO_3 (1:1), and add the recovered copper and lead to the filtrate reserved in accordance with Paragraph (*a*).

(*c*) An alternative method[16] for recovering copper and lead is to return the metastannic acid and paper obtained in accordance with Paragraph (*a*) to the original beaker, add 15 to 20 ml of HNO_3 and 10 to 15 ml of $HClO_4$, and heat to copious white fumes to destroy organic matter. Cool somewhat, wash the cover glass and sides of the beaker, and add 15 to 25 ml of HBr. Heat to copious white fumes to volatilize tin, arsenic, and antimony. If the solution is not clear, repeat the treatment with HBr. Evaporate the solution to near dryness, dissolve the residue in a few milliliters of HNO_3 (1:1), and add the recovered copper and lead to the filtrate reserved in accordance with Paragraph (*a*).

(*d*) Add 1 drop of 0.1 *N* HCl to the solution and dilute to 150 ml. Insert the electrodes into the solution, cover with a pair of split watch glasses, and electrolyze overnight at a current density of 0.5 amp. per sq. dm. or for 2.5 hr. at a current density of 4 amp. per sq. dm.[17] The more rapid procedure requires the use of gauze cathodes. When the solution is colorless, wash down the cover glasses, electrodes, and the sides of the beaker, and continue the electrolysis until deposition of the copper is complete, as indicated by failure to plate on a new surface when the level of the solution is raised. When no copper appears, it can be assumed that all the lead has also been deposited.[18] The electrolyte may be reserved for the determination of zinc (Section 16), aluminum (Section 22), or nickel (Section 25).

(*e*) When deposition of the copper is complete, with the current still on, lower the beaker slowly, while washing the cathode with water. Remove the cathode, rinse it in water, and dip it in two successive baths of ethanol or methanol. Dry in an oven at 110°C for 3 to 5 min., cool, and weigh the deposit as metallic copper.

(*f*) Remove the anode, rinse thoroughly with water, and dry at 110 to 120° for 30 min. The deposit is fragile and must be handled carefully. Cool the anode and weigh the deposit as PbO_2.

[16] This procedure is not suitable for the analysis of phosphor bronze.

[17] When agitation of the electrolyte is permissible in order to decrease the time of deposition, one of the types of rotating forms of electrodes generally available may be employed.

[18] If the electrolyte is not to be used for subsequent determinations, remove a few drops of the solution, place on a porcelain spot plate, and treat with saturated H_2S solution. Continue electrolysis until no CuS precipitate is observed.

(*g*) *Calculation.* Calculate the percentages of copper and lead as follows:

$$\text{Copper, per cent} = \frac{A}{B} \times 100$$

$$\text{Lead, per cent} = \frac{C \times 0.866}{B} \times 100$$

where,

A = grams of copper,
B = grams of sample used, and
C = grams of PbO_2.

(*h*) If manganese is present in the alloy, a part of it may co-deposit with the PbO_2. In this event, after the anode is removed from the electrolysis terminal, transfer it to a 250-ml beaker, dissolve the deposit in HNO_3 (1:1) containing a few drops of ethanol, wash the anode thoroughly, and remove it from the beaker. Add 35 ml of "lead acid" solution and evaporate on the hot plate to dense white fumes. Allow to cool, add 30 ml of water, bring to a boil and allow to stand 1 to 2 hr. Filter the solution through a tared asbestos Gooch crucible and wash the precipitate with cool "lead acid." Heat the precipitate of $PbSO_4$, gently at first, and then to constant weight at very dull redness (500 to 600°C) by suspending the crucible in a larger one so that an air space separates the two.

(*i*) *Calculation.* Calculate the percentage of lead as follows:

$$\text{Lead, per cent} = \frac{A \times 0.6833}{B} \times 100$$

where,

A = grams of $PbSO_4$, and
B = grams of sample used.

Procedure for Copper-Silicon Alloys

7. (*a*) Transfer 2.000 g of the sample to a covered 250-ml beaker, add 25 ml of HNO_3 (1:1),[10] and boil gently or allow to remain on a steam bath until dissolution is complete and brown fumes have been expelled. Cool somewhat, and wash down the cover glass and sides of the beaker with water. With the aid of an acid-resistant plastic dropper, add HF drop by drop until the silicic acid gel is converted to H_2SiF_6 and the solution is clear. If no lead is present in the alloy, add 3 ml of $Pb(NO_3)_2$ (10 g per l), as in electrolyzing it is necessary that the anode be covered by a coating of PbO_2 in order to prevent a slight attack by HF.

[10] If tin is present in the alloy, add 3 to 5 ml of HF to the HNO_3 (1:1) before adding it to the sample.

(*b*) Electrolyze the solution and complete the determination as described in Section 6 (*d*) to (*e*). If manganese is present in the alloy, determine the lead by precipitation as $PbSO_4$ as described in Section 6 (*h*) and (*i*).

Lead by Electrodeposition as the Dioxide

Apparatus

8. *Electrodes for Electroanalysis.* Either stationary or rotating type.

Procedure for Alloys Containing Under 6.0 per cent of Lead, Under 0.05 per cent of Tin, and Under 0.01 per cent of Phosphorus.

9. (*a*) *Solution of Samples Containing Under 1.0 per cent of Lead.* Transfer 5.0 g of the sample to a 250-ml beaker, cover, and dissolve in 50 ml of HNO_3 (1:1). If silicon is present in the alloy, add sufficient HF to clear the solution.

(*b*) *Solution of Samples Containing 1.0 to 6.0 per cent of Lead.* Transfer 1.000 g of the sample to a 250-ml beaker, cover, and dissolve in 20 ml of HNO_3 (1:1). If silicon is present in the alloy, add sufficient HF to clear the solution.

(*c*) After dissolution is complete, boil the solution gently to expel brown fumes, and allow to cool slightly. Wash down the cover glass and the sides of the beaker, and dilute to 150 ml.

(*d*) Insert the electrodes into the solution, cover with a pair of split watch glasses, and electrolyze for 1 hr. at a current density of 1.25 to 1.50 amp. per sq. dm. Wash down the cover glasses, electrodes, and sides of the beaker, and continue the electrolysis until no darkening of the platinum can be detected when the current has been continued for 15 min. after the level of the liquid has been raised.

(*e*) When deposition of the lead is complete, without interrupting the current, siphon off the electrolyte at the same time filling the beaker with water. Remove the anode quickly, rinse thoroughly with water, and dry at 110 to 120° for 30 min. The deposit is fragile and must be handled carefully. Cool the anode and weigh the deposit as PbO_2.

(*f*) *Calculation.* Calculate the percentage of lead as follows:

$$\text{Lead, per cent} = \frac{A \times 0.866}{B} \times 100$$

where,

A = grams of PbO_2, and
B = grams of sample used.

Lead by Precipitation as the Sulfate

Apparatus

10. *Gooch Crucible.* Usual type, heated at 600°C.

Procedure for Alloys Containing 6.0 per cent and Over of Lead

11. (*a*) Transfer 1.000 g of the sample to a 250-ml beaker, cover, and add 15 ml of HNO_3 (1:1). Heat on a steam bath until dissolution of the sample is complete, add 50 ml of hot water, and digest on a steam bath for 1 to 2 hr. If tin is present, filter off the metastannic acid, remove the tin, and combine the filtrate and recovered lead as described in Section 6 (*b*) or (*c*).

(*b*) If silicon is not present in the alloy, add 20 ml of H_2SO_4 (1:1) to the solution obtained in accordance with Paragraph (*a*), transfer to a hot plate, and evaporate to dense white fumes. If silicon is present in the alloy, transfer the solution to a platinum dish, add sufficient HF to volatilize the silicon, add 20 ml of H_2SO_4 (1:1), transfer to a hot plate, and evaporate to dense white fumes. Cool, wash down the sides of the beaker or platinum dish with water, and again evaporate to dense white fumes. Dilute to 150 ml, allow to stand for 1 to 2 hr., filter through a tared Gooch crucible, and wash the precipitate with cool water. Reserve the filtrate and washings.[20]

Heat the precipitate of $PbSO_4$, gently at first, and then to constant weight at very dull redness (500 to 600°) by suspending the crucible in a larger crucible, so that an air space separates the two.

(*d*) *Calculation.* Calculate the percentage of lead as follows:

$$\text{Lead, per cent} = \frac{A \times 0.6833}{B} \times 100$$

where,

A = grams of $PbSO_4$, and
B = grams of sample used.

Tin by Titration with Iodine

Apparatus

12. *Apparatus for Reduction of Tin.* When tin is to be reduced to the stannous state and determined by titration with standard iodine or

[20] If a value of greater accuracy is desired, very small amounts of residual lead may be recovered by electrolysis from the filtrate and washings, reserved in accordance with Section 11 (*b*). Add 2 ml of HNO_3 to the solution and electrolyze, using a weighed gauze anode. Weigh the PbO_2, calculate to lead, and add the recovery to the lead already found as sulfate.

iodate solution, air must be excluded during the reduction and titration to prevent oxidation of the stannous tin. For work of high accuracy, it is best to keep the tin solution under gaseous CO_2. Figure 31.1 shows one of the many forms of apparatus that may be used when gaseous CO_2 is employed. It shall consist of a flask closed with a three-hole rubber stopper containing an inlet tube for CO_2, an air condenser, and a hole for the buret (glass plugged). During reduction a very slow stream of CO_2 shall be passed through the flask. When reduction is complete, the flow shall be increased to maintain a protecting blanket of CO_2 during the cooling and titration.

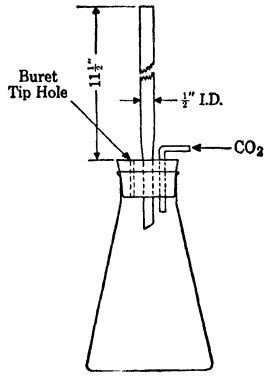


Figure 31.1

Apparatus for reduction of tin.

Reagents

13. (*a*) *Ferric Chloride Solution* (*10 g per l*). Dissolve 10 g of $FeCl_3 \cdot 6\,H_2O$ in water and dilute to 1 liter.

(*b*) Test Lead.

(*c*) *Iron.* Relatively pure iron (not less than 99.85 per cent Fe). Wire, strap, or rod may be used.

(*d*) *Nickel.* A roll of nickel sheet having an exposed area of at least 10 sq. in.

(*e*) *Aluminum.* Sheet or rolled foil of aluminum.

(*f*) *Antimony Chloride Solution* (*20 g per l*). Dissolve 2 g of $SbCl_3$ in 50 ml of HCl, and dilute to 100 ml with water.

(*g*) *Potassium Iodide Solution* (*100 g per l*). Prepare fresh as required.

(*h*) *Starch Solution* (*10 g per l*). Reagent No. 110.

(*i*) *Standard Tin Solution* (*1 ml = 0.001 g Sn*). Reagent No. 19.

(*j*) *Standard Iodine Solution* (*1 ml = 0.003 g Sn, approximately 0.05 N*). Reagent No. 7. Standardize the iodine solution as follows: Pipet 50 ml of the tin solution (1 ml = 0.001 g Sn) into a 300-ml Erlenmeyer flask, add reagents, and reduce the tin as described in Section 14 (*c*), (*d*), (*e*), or (*f*). Continue the standardization and titrate with the iodine solution as described in Section 14 (*g*).

(*k*) *Standard Potassium Iodate Solution* (*1 ml = 0.003 g Sn, approximately 0.05 N*). Reagent No. 12. Standardize the KIO_3 solution as prescribed for the iodine solution in Paragraph (*j*).

Procedure

14. (*a*) Transfer 1.000 to 2.000 g of the sample, depending on the tin content, to a 250-ml beaker, cover, and dissolve in 5 ml of HCl and 20 ml of HNO_3 (1:1), adding more HCl, if necessary, to keep the tin in solution. Heat on a steam bath until dissolution of the sample is complete and brown fumes have been expelled.[21] Wash down the cover glass and sides of the beaker, and dilute to 125 ml with water. If there is not sufficient iron in the alloy to gather the tin hydroxide when precipitated with NH_4OH, add 5 to 10 ml of $FeCl_3 \cdot 6\ H_2O$ (10 g per l).

(*b*) Neutralize with NH_4OH, and add a slight excess. Bring the solution to incipient boiling. Filter through a rapid paper, and wash the beaker and precipitate several times with hot NH_4Cl (10 g per 1). Discard the filtrate and washings, place the original beaker beneath the funnel, and dissolve the precipitate through the paper with hot HCl (1:1). Wash the paper several times with hot water and retain it in the funnel for the next filtration. Reprecipitate with NH_4OH, boil, filter, and wash thoroughly with NH_4Cl (10 g per l), until all nitrates have been removed. Remove the paper and precipitate from the funnel and place it in a 500-ml Erlenmeyer flask. Reduce the solution as described in Paragraph (*c*), (*d*), (*e*), or (*f*).

(*c*) *Reduction with Lead.* Add 200 ml of water to the Erlenmeyer flask containing the paper and precipitate. Add 75 ml of HCl, 2 drops of $SbCl_3$ (20 g per l) and 5 g of test lead, and swirl the flask to break up the paper and to aid in the dissolution of the precipitate. Stopper the flask as described in Apparatus No. 7B. Heat the solution to boiling, and boil at a moderate rate for 1 hr.

(*d*) *Reduction with Iron.* Add 200 ml of water to the Erlenmeyer flask containing the paper and precipitate. Add 60 ml of HCl, 2 drops of $SbCl_3$ (20 g per l), and at least 5 g of iron, and swirl the flask to break up the paper and to aid in the dissolution of the precipitate. Stopper the flask as described in Apparatus No. 7B. Heat the solution to boiling, and boil with continuous evolution of gas for at least 30 min. Some undissolved iron should remain after the reduction.

(*e*) *Reduction with Nickel.* Add 200 ml of water to the Erlenmeyer flask containing the paper and precipitate. Add 75 ml of HCl and 2 drops of $SbCl_3$ (20 g per l), introduce a roll of sheet nickel, and swirl the flask to break up the paper and aid in dissolution of the precipitate.

[21] If appreciable amounts of silicon or lead, or both, are present, remove the silicon by volatilization with HF and H_2SO_4, and remove the lead as $PbSO_4$, by precipitation and filtration.

Stopper the flask as described in Apparatus No. 7B. Heat the solution to boiling, and boil with continuous evolution of gas for at least 45 min.

(*f*) *Reduction with Aluminum.* Add 100 ml of cold water to the Erlenmeyer flask containing the paper and precipitate. Add 80 ml of HCl and 2 drops of $SbCl_3$ (20 g per l), and introduce about 2 g of aluminum into the cool solution. When the aluminum is nearly dissolved, stopper the flask as described in Apparatus No. 7B. Heat the solution to boiling, and boil for 10 to 15 min. (until all the aluminum and metallic tin are in solution).

(*g*) After reduction is complete, cool the contents of the flask to about 10°C, if reduced with lead, iron, or nickel, and to 25°C if reduced with aluminum, maintaining an atmosphere of CO_2 by passing CO_2 into the flask. Add 5 ml of KI (100 g per l) and 5 ml of starch solution (10 g per l) and titrate with either iodine (1 ml = 0.003 g Sn)[22] or KIO_3 (1 ml = 0.003 g Sn) to a persistent blue tint.

(*h*) *Blank.* Make a blank determination, following the same procedure and using the same amounts of all reagents.

(*i*) *Calculation.* Calculate the percentage of tin as follows:

$$\text{Tin, per cent} = \frac{(A - B)C}{D} \times 100$$

where,

A = milliliters of iodine or KIO_3 solution required to titrate the sample,
B = milliliters of iodine or KIO_3 solution required to titrate the blank,
C = tin equivalent of the iodine or KIO_3 solution, in grams per milliliter, and
D = grams of sample used.

Zinc by Precipitation as Sulfide

Reagents

15. (*a*) *Hydrogen Sulfide Wash Solution.* Add 10 ml of H_2SO_4 to 1 liter of water and saturate with H_2S.

(*b*) *Uranyl Nitrate Indicator Solution.* Dissolve 5 g of $UO_2(NO_3)_2 \cdot 6\ H_2O$ in water and dilute to 100 ml.

(*c*) *Standard Potassium Ferrocyanide Solution (1 ml = 0.01 g Zn).* Reagent No. 11. Standardize[23] the $K_4Fe(CN)_6$ solution as follows:

[22] In the analysis of alloys low in tin, iodine (1 ml = 0.001 g Sn, approximately 0.02 *N* or KIO_3 (1 ml = 0.001 g Sn, approximately 0.02 *N*) may be substituted for the solutions prescribed in Section 14 (*g*).

[23] Each operator should standardize his own solutions. One or two standards should be carried along with each lot of zinc determinations. While ferrocyanide solutions do not change much, there is quite a difference in the ability of operators to catch the end point. If the standardizations are made on about the same weight of zinc as that in the sample under analysis, corrections for end points are unnecessary.

Transfer an amount of metallic zinc approximately equal to that in the sample to a 600-ml beaker, dissolve in 20 ml of HCl (1:1), and dilute to 300 ml with hot water. Add 10 g of NH_4Cl and 2 to 3 ml of H_2S wash solution, and titrate with the $K_4Fe(CN)_6$ solution as described in Section 16 (*i*).

Procedure[24]

16. (*a*) If the zinc content of the sample is 1 per cent or over, and the electrolyte has been reserved for the zinc determination in accordance with Section 6 (*d*), proceed as described in Paragraph (*c*). If the electrolyte is not available, transfer 1.000 to 4.000 g of the sample, containing 0.04 to 0.4 g of zinc, to a 250-ml beaker and proceed as described in Paragraph (*b*).

(*b*) If the zinc content of the sample is under 1 per cent, transfer 5.0 g of the sample to a 250-ml beaker, and treat in accordance with Section 6 to dissolve the sample[25] and to remove copper, lead, tin, antimony, and arsenic, using amounts of reagents appropriate to the size of sample taken.

(*c*) To the electrolyte reserved in accordance with Section 6 (*d*) or obtained in accordance with Paragraph (*b*) add 15 ml of H_2SO_4 (1:1) and evaporate to dense white fumes. Cool the solution. If silica is present, dilute to approximately 50 ml, filter through a close-texture paper into a 400-ml beaker, and wash thoroughly with H_2SO_4 (1:99). Dilute to 200 ml.

(*d*) Cool to room temperature and pass in a rapid stream of H_2S for 15 min. This treatment with H_2S removes the last traces of copper and lead, if any are present, and also tin, arsenic, and antimony. Allow to stand for 2 hr. and filter through a close-texture paper into a 600-ml beaker. Wash thoroughly with H_2S wash solution. If the electrolyte from the copper or lead determination is being used and a noticeable amount of copper or lead, or both, is found in the precipitate, dissolve the precipitate in HNO_3 (1:3), electrolyze the solution, and add to the previously obtained values the recovered amounts of copper and lead. Otherwise, discard the precipitate.

(*e*) Boil the filtrate and washings for 25 to 30 min. to remove H_2S. Cool the solution, carefully neutralize with NH_4OH (1:2), using methyl orange indicator, and dilute to 400 ml. Add 1 ml of 1 *N* H_2SO_4 for each

[24] If the ferrocyanide method is to be used, 0.1 g or more of zinc must be present or the end point will not be clear. The upper limit is generally regarded as 0.6 g of zinc.

[25] If an appreciable amount of silicon is present, volatilize it by treating with HF and H_2SO_4 in a platinum dish. Return the contents of the dish to the original beaker and treat with HBr to volatilize any tin, antimony, or arsenic. Dilute and, if $PbSO_4$ is present, filter. Add 2 ml of HNO_3 and electrolyze.

100 ml of solution so that the solution has an acidity of 0.01 *N*. Cool the solution to room temperature, and pass in a rapid stream[26] of H_2S for at least 30 min.

(*f*) Allow the white precipitate of ZnS to settle, and filter through a close-texture ashless paper. Wash the precipitate thoroughly with cold water to remove all traces of soluble salts. Clean the beaker thoroughly with a policeman to remove all adhering ZnS, and complete the determination by the oxide method as described in Paragraphs (*g*) and (*h*) or by the ferrocyanide method as described in Paragraphs (*i*) and (*j*).

Oxide Method

(*g*) Transfer the paper and precipitate to a weighed porcelain crucible, dry on a hot plate, and heat cautiously to ignite the paper, taking care that the sulfur fumes do not ignite. Finally, place the crucible and contents in an electric muffle, and heat at a temperature of 950°C for 15 min. Cool and weigh as ZnO. Heat again in the muffle for 10 min., cool, and weigh. Repeat the heating until constant weight is obtained.

(*h*) *Calculation.* Calculate the percentage of zinc as follows:

$$\text{Zinc, per cent} = \frac{A \times 0.8034}{B} \times 100$$

where,

A = grams of ZnO, and
B = grams of sample used.

Ferrocyanide Method

(*i*) Transfer the paper containing the ZnS precipitate to the original beaker (Paragraph (*f*)), cover, and digest with 20 ml of HCl (1:1). Wash down the cover glass and sides of the beaker, dilute to 300 ml with hot water, add 10 g of NH_4Cl, and warm to 80°C. Titrate with $K_4Fe(CN)_6$ (1 ml = 0.01 g Zn) using uranyl nitrate on a spot plate as an outside indicator. The end point is the appearance of the insoluble red-brown uranyl ferrocyanide which forms with the first excess of $K_4Fe(CN)_6$.

(*j*) *Calculation.* Calculate the percentage of zinc as follows:

$$\text{Zinc, per cent} = \frac{AB}{C} \times 100$$

where,

A = milliliters of $K_4Fe(CN)_6$ solution required to titrate the sample,
B = Zinc equivalent of the $K_4Fe(CN)_6$ solution, in grams per milliliter, and
C = grams of sample used.

[26] In precipitating zinc with H_2S, the gas should pass through the solution at a rate of at least 6 bubbles per second.

Nickel by Precipitation as the Dimethylglyoxime Complex

Apparatus

23.[27] *Filtering Crucible.* A Gooch crucible or a fritted-glass crucible of medium porosity (Apparatus No. 2).

Reagents

24. (*a*) *Tartaric Acid Solution (250 g per l).*

(*b*) *Alcohol Solution of Dimethylglyoxime (10 g per l).* Reagent No. 104.

Procedure

25. (*a*) If the electrolyte reserved in accordance with Section 6 (*d*) is available, it or an aliquot containing under 0.05 g of nickel may be used. If a separate sample is taken, use a 2.00-g portion for samples containing under 2.0 per cent of nickel, or use a 1.000-g portion for samples containing 2.0 to 5.0 per cent of nickel. Transfer to a 250-ml beaker and treat to dissolve the sample and to remove the copper, in accordance with Section 6 (*a*) and (*d*) or Section 7 (*a*) and (*b*).

(*b*) If silicon is present in the alloy, add 5 ml of H_2SO_4 to the electrolyte and evaporate to dense white fumes. Cool, dilute, and filter through a close-texture paper. Wash thoroughly with H_2SO_4 (3:97). Dilute to 100 to 300 ml, depending on the nickel content.

(*c*) Transfer the solution to a 400-ml beaker and add 10 ml of tartaric acid (250 g per l). Neutralize with NH_4OH and add 1 ml in excess. Heat to 70°C, and add 0.4 ml of the alcohol solution of dimethylglyoxime (10 g per l) for each 1 mg of nickel present and 5 to 10 ml in excess, pouring directly into the solution and not down the beaker wall. Stir the mixture vigorously, and allow to cool to room temperature, while stirring occasionally.[28] Filter, using a weighed Gooch crucible or a fritted-glass crucible of medium porosity, and wash well with cold water.

(*d*) Dry the precipitate at 150°C to constant weight. Cool in a desiccator and weigh as nickel dimethylglyoxime.

(*e*) *Calculation.* Calculate the percentage of nickel as follows:

$$\text{Nickel, per cent} = \frac{A \times 0.2032}{B} \times 100$$

[27] Section Numbers 17 to 22 and 29 to 49, inclusive, are omitted. They cover various methods for the determination of Al, As, Mn, P, Sb, Si, and Sn. [*Author*]

[28] If the percentage of nickel is very low, the solution should be allowed to stand overnight. In such cases the precipitate is frequently contaminated by dimethylglyoxime and so it is best to filter, dissolve the precipitate in a small amount of HCl, and reprecipitate the nickel in a small volume, using only 1 or 2 ml of dimethylglyoxime (10 g per l).

where,

A = grams of nickel dimethylglyoxime, and
B = grams of sample used.

Iron by Titration with Dichromate

Reagents

26. (*a*) *Stannous Chloride Solution* (*50 g per l*). Dissolve 12.5 g of $SnCl_2 \cdot 2\ H_2O$ in 25 ml of HCl, and dilute to 250 ml. Keep the solution in a well-stoppered bottle.

(*b*) *Mercuric Chloride Solution* (*saturated*). Add 60 to 100 g of $HgCl_2$ to 400 ml of hot water, shake, and cool to room temperature. More water may be added from time to time as long as crystals remain undissolved.

(*c*) *Sodium Diphenylaminesulfonate Indicator Solution* (*2 g per l*).

(*d*) *Standard Potassium Dichromate Solution* (*0.05 N*). Reagent No. 10.

Procedure for Alloys Containing Under 0.05 per cent of Tin, Under 0.01 per cent of Arsenic, and Under 0.01 per cent of Antimony.

27. (*a*) If the iron content is under 0.25 per cent, transfer 5.0 g of the sample, from which adventitious iron has been removed, to a 400-ml beaker and dissolve in 50 ml of HNO_3 (1:1). If the iron content is 0.25 per cent or over, transfer 1.00 to 2.00 g of the sample, from which adventitious iron has been removed, to a 250-ml beaker and dissolve in 25 ml of HNO_3 (1:1).

(*b*) If silicon is present, add a few drops of HF to decompose any iron silicide. Add 5 to 10 ml of H_2SO_4 and evaporate to dense white fumes. Allow to cool, dilute somewhat with water, and filter if necessary. Add 2 to 3 ml of HNO_3, and boil for 5 min.

(*c*) Dilute the solution to 150 ml. Add NH_4OH until slightly but distinctly alkaline, and boil gently for a few minutes. Remove the beaker from the hot plate, allow the precipitate to settle for a few minutes, and filter while hot, using a medium-texture paper. Wash the beaker and precipitate a few times, alternately with NH_4Cl (20 g per l) and hot water, to remove most of the soluble salts.

(*d*) Dissolve the precipitate through the paper with 20 ml of hot HCl (1:1) and wash thoroughly with hot water to remove the last traces of iron, collecting the solution and washings in the original beaker. Proceed as described in Paragraph (*c*). Dissolve the precipitate through

the paper with 20 ml of hot HCl (1:1) and wash thoroughly with hot water, collecting the solution and washings in the original beaker.

(*c*) Evaporate the solution to 15 to 20 ml and wash down the sides of the beaker. Heat to boiling, and add $SnCl_2 \cdot 2\ H_2O$ (50 g per l) drop by drop, while swirling the beaker over a white background, until the yellow color of the $FeCl_3$ disappears. Add 1 drop of $SnCl_2$ solution in excess, but no more.

(*f*) Dilute the reduced solution to 50 ml, cool to room temperature, stir, and add at one stroke 10 ml of a saturated solution of $HgCl_2$. The resultant precipitate should be pure white in color, and in amount should be preferably not more than enough to give a pearly opalescence. If the precipitate is gray or dark, too large an excess of $SnCl_2$ has been used and it will be necessary to discard the solution and start anew. To the properly reduced solution, add 10 ml of H_3PO_4 (1:3) and 4 drops of sodium diphenylaminesulfonate indicator (2 g per l).

(*g*) The volume of the solution to be titrated should not exceed 100 ml. Titrate slowly with 0.05 *N* $K_2Cr_2O_7$, while stirring constantly, until the color of the solution changes from green to a gray-green. Continue the titration, drop by drop, until the first tinge of purple or violet-blue appears.

(*h*) *Blank.* Make a blank determination, following the same procedure and using the same amounts of all reagents.[29]

(*i*) *Calculation.* Calculate the percentage of iron as follows:

$$\text{Iron, per cent} = \frac{(A - B)C \times 0.0559}{D} \times 100$$

where,

A = milliliters of $K_2Cr_2O_7$ solution required to titrate the sample,
B = milliliters of $K_2Cr_2O_7$ solution required to titrate the blank,
C = normality of the $K_2Cr_2O_7$ solution, and
D = grams of sample used.

Procedure for Alloys Containing 0.05 per cent and Over of Tin, With or Without Arsenic and Antimony.

28. (*a*) It is desirable to remove the tin to facilitate later handling. Arsenic and antimony, if present, must be removed, since they interfere in the titration.

(*b*) Transfer 5.0 g of the sample, from which adventitious iron has been removed, to a 250-ml beaker. Add 50 ml of HNO_3 (1:1), and heat

[29] Ferric iron must be present in the solution in order to obtain the purple or violet-blue end-point color. If the color fails to form, the blank is less than the equivalent of 1 drop of 0.02 *N* $FeSO_4$, as this contains sufficient iron to yield an end-point.

to expel brown fumes. If silicon is present, add a few drops of HF to decompose any iron silicide. Dilute the solution to 100 ml with hot water and digest the metastannic acid on a steam bath for 1 hr. Filter through double, close-texture papers into a 400-ml beaker, wash with hot HNO_3 (1:99), and reserve the filtrate. If HF has been used, add 5 to 10 ml of H_2SO_4 and evaporate to dense white fumes. Cool, dilute, and filter if necessary.

(*c*) Transfer the paper and contents to the original beaker. Add 15 ml of HNO_3 and then 10 ml of $HClO_4$. Heat gently until white fumes appear, cool, and wash down the sides of the beaker. Cover, and add 10 ml of HBr. Remove the cover glass and boil gently until white fumes appear. Repeat the HBr treatment to expel the last traces of tin and antimony. Add 15 ml of water and heat to dissolve soluble salts. If SiO_2 is present, filter the solution, and combine with the filtrate reserved in accordance with Paragraph (*b*). Complete the determination of iron in accordance with Section 27 (*c*) to (*i*).

CHAPTER 32

LIBRARY PROBLEM

Mere use of a method of analysis devised by others seems insufficient in most cases to impress students with the reasons for, and the importance of, many of the details in an involved procedure. The relevancy of some of the details in a method of analysis may be emphasized by assigning to the student the problem of designing a method for a hypothetical situation. The procedure he recommends must be based on facts to be found in the literature.

This kind of library problem necessitates collecting specific information on the chemistry involved in any preliminary treatment and/or separation of each constituent, together with the physics of possible methods of measurement. Then follows the solution of the puzzle, that is, formulating what seems likely to be a workable procedure for determining each of the desired constituents. The general aspects of such a problem have been presented elsewhere.[1]

DETAILS TO BE CONSIDERED

The operating details of a method of analysis designed for determining several constituents in a given substance will depend on a number of factors.

Very small amounts of available material may necessitate micro- or even ultramicromethods. Otherwise, macromethods are generally less exacting in requirements of skill and equipment.

Devising a polycomponent procedure for the determination of desired constituents presupposes knowledge of the constituents present and of their chemical properties. Each chemical element, radical, and compound has its own individual properties in terms of which the analytical method must be devised.

[1] Mellon, *J. Chem. Educ.* **24**, 283 (1947).

Whether each constituent is present in major or trace amounts must be known or determined before the most suitable method of analysis can be devised. In general, methods applicable for trace amounts of constituents are unsuited for the determination of a component present in major amount. Thus, polarographic methods are usually at their best for constituents in a concentration of about 10^{-4} M.

If nothing less than the highest obtainable accuracy will suffice, the method capable of yielding such results is imperative. Often, however, such data are not worth while, in which case a less exacting method should be chosen.

Ever increasing speed is the dominant factor in much of industry. To the extent that its reliability will suffice, the most rapid method is desirable.

Often methods of separation and/or measurement require expensive apparatus and unusual operating facilities, e.g., direct-reading emission spectrometers and vacuum fusion apparatus. Recommendation of methods requiring such apparatus is not feasible for many laboratories.

Measurements employing involved chemical transformations and intricate measuring apparatus necessitates more competent personnel than simpler procedures. As a rule, the simpler the measuring equipment and the process of treatment and separation, the more easily the whole method may be routinized for determinator personnel.

SUGGESTED PROBLEM

As a beginning problem, it is instructive to devise a procedure for a hypothetical alloy. The specific assignments should take into account the state of chemical knowledge and the experience of the student. Where such background is adequate, the following combinations are suggested as examples of hypothetical alloys that may be used as problems:

Cd, Ge, Li, Sc	Na, Se, Zn, Y
Be, Mo, Sr, K	Fe, Ra, Rb, Th
Al, Cs, La, W	Cu, In, Sb, Ti
Ag, Ce, Ga, Ni	Co, Mg, Sn, Zr
Ca, Cb, Pb, Re	As, Ba, Tl, U

Mixtures of other kinds of substances may be assigned. The possibilities in organic chemistry, particularly, are almost limitless. Some organic problems are easy. An example is the separation by volatilization of four liquids having boiling points far apart, and the volumetric measurement of the distillates. Many organic mixtures are extremely

difficult. Also the relevant literature for such organic analytical problems is not easily found.

FACTUAL DATA NEEDED

After a problem has been assigned, the student must seek out factual information on possible methods of handling the combination of constituents involved in his problem. The most generally useful reference sources for this information are monographs and treatises, some of which are listed at the end of this chapter. Occasionally, useful facts may be found in the more comprehensive textbooks on quantitative analysis.

Whatever the sources used, the relevant facts that must be ascertained for each constituent concern its chemistry and methods for its measurement. Of chief chemical importance are the reactions and means that may be used to effect any necessary preliminary treatment and/or separations, e.g., dissolution, change of oxidation state, formation of complexes, and separation by appropriate means. Of chief physical interest are the methods of measurement applicable to the constituents included.

SELECTION OF METHODS

For each constituent in the sample a separate list should be made of the possibilities of preliminary treatment (such as appropriate solvents), separation, and measurement. From these possibilities a selection must then be made of the combined methods that seem most likely to be workable for the sample as a whole. The final procedure should be (1) applicable to the constituents present and the relative amounts under consideration, (2) capable of yielding results of the desired reliability, (3) as rapid as possible without sacrificing desired reliability, and (4) feasible with the apparatus and facilities at hand.

For a quaternary alloy, such as those suggested, certain kinds of measurements on the sample as such are inapplicable. Thus, no single measurement of a property, such as mass, can provide data for calculating four unknowns. If the minimum percentage of each element is specified as 20, methods for trace amounts of constituents are eliminated.

The number of samples needed (disregarding checks) depends on subsequent operations. One sample will suffice if the procedure involves separating each constituent in turn before measurement. If each constituent can be measured in the presence of the other three, thus avoiding necessity for separations, much time can be saved by starting with four samples. Few manual operations require less time than weighing with a damped chainomatic balance, or one of the newer projection types.

Dissolution of the sample is the most generally promising approach to

the handling of such an alloy. Usually the solvent will be an acid or a mixture of two or more acids. Analysts generally prefer to dissolve a sample completely before starting separations or measurements. Occasionally, as in the treatment of a bronze with nitric acid, one constituent is converted in the dissolution process into an insoluble compound that can then be removed by filtration. In general, this kind of selective dissolution, leaving one or more elements undissolved, has not been found applicable in metallurgical work. However, it is widely used in food and drug work.

Having ascertained possible solvents for each element, the student should select the medium that will best expedite subsequent operations. Thus, if the alloy should be soluble in several different acids, including nitric, and if lead is to be separated by electrodeposition, nitric acid would be the choice. In some other situations the presence of nitric acid might be quite undesirable.

If measurement has been narrowed down to gravimetric and titrimetric methods, probably first consideration should go to the possibilities of titration. First choice would be a procedure involving the use of four samples and the titration of each constituent in the presence of the other three, thus avoiding any separations. The measurement may be titrimetric, of course, even though a prior separation is necessary.

If measurement without prior separation seems unfeasible, attention must be directed to methods for getting the elements apart. Procedures most likely to work are summarized in Chapters 7-10. The best selection depends on the properties of the constituents composing the sample.

In recommending specific reagents, consideration should be given to avoiding complications in subsequent operations. For example, a precipitant for a given constituent may react with more than one ion, or its excess may not easily be removed, if necessary, to prevent some later interference. This necessity to avoid later complications should impress the method-builder with the wisdom of using, if possible, reagents such as ammonia, ammonium salts, hydrogen peroxide, bromine water, and hydrogen sulfide. Excess of such reactants may usually be eliminated without difficulty.

It is not desirable in careful work to determine three of the four elements and then take the fourth by difference. Errors cumulating on the three are then attached to the fourth.

FORM OF REPORT

The written report should list first, for each constituent assigned, the methods of separation and measurement which the reference sources

indicate are most likely to be usable for the percentage ranges specified.

Next, the report should contain the general statement of the procedure recommended for determining each constituent, preferably in the form used in this book (see procedure for analysis of brass, page 587). This form consists essentially of the following different parts: (1) the synoptic statement of the general principle of the procedure; (2) the operating procedure, insofar as this can be settled without actual laboratory trial; (3) the explanatory and precautionary notes relating to separate steps in the procedure; and (4) the block outline or flow sheet showing the major steps.

SELECTED LITERATURE REFERENCES [2]

Original Sources

1. PERIODICALS: PAPERS ON THEORETICAL AND APPLIED ANALYSIS

Analyst, The[3]
Analytica Chimica Acta
Analytical Chemistry[4]
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Annales des falsifications et des fraudes
Información de quimica analytica
Journal of the **Association of Official Agricultural Chemists**
Mikrochemie vereinigt mit Mikrochemica Acta
Spectrochimica Acta
Zavodskaya Laboratoriya
Zeitschrift für analytische Chemie
Zhurnal Analiticheskoĭ Khimii

See also journals of the general chemical societies, and some trade journals.

2. GOVERNMENT BULLETINS:

Many papers from government laboratories appear in the appropriate journals. Often such material is issued as separate bulletins, especially from sources such as the National Bureau of Standards, the Bureau of Mines, the Bureau of Agricultural Chemistry and Engineering, and the National Institutes of Health.

3. PATENTS:

A few patents deal with analytically important machines (instruments), processes, and products.

4. MANUFACTURERS' TECHNICAL PUBLICATIONS:

Examples are the bulletins of the G. Frederick Smith Chemical Co. and the Solvay Process Co.

[2] See Mellon, *Chemical Publications*, McGraw-Hill, 1940.
[3] The boldface part of the name is the abbreviation used in *Chemical Abstracts*.
[4] Formerly *Analytical Edition of Industrial and Engineering Chemistry*.

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[5] These textbooks are merely a sampling of the several dozen available.

PART THREE

Numerical Analytical Problems

CHAPTER 33

TYPICAL PROBLEMS AND THEIR SOLUTION

In general, two rather distinct kinds of numerical problems are of interest to the student of quantitative chemical analysis and to the practicing analyst. Of these two types, one is predominantly theoretical in nature, and the other is perhaps even more predominantly practical in nature.

The first type of problem represents, in essence, the application of simple physical chemistry to the systems involved. Familiar topics involving ionic equilibria are solubility, solubility product, common and diverse ion effects, ionization, *p*H, buffers, hydrolysis, complexation, instability, oxidation-reduction, and others. Such problems have long been considered basic in the more comprehensive texts on inorganic qualitative analysis. Consequently, in this book no effort has been made to cover all this material again.[1] The subjects are equally important in qualitative and quantitative analysis, but no book of acceptable size can include everything.

The second type of problem deals primarily with the kind of calculations that have to be made in the course of performing analyses. For example, materials are weighed, vessels calibrated, titrations made, and amounts of desired constituents calculated. To be able to calculate the *p*H of a buffer, or the equilibrium constant of a given system, is highly desirable; but to be able to make the calculations necessary for an analysis is indispensable, if the results are to be useful. Because of its great practical importance, therefore, this second type of problem is emphasized here.

[1] Instructors who wish to include such problems in the quantitative course may find many of them in the better textbooks on qualitative analysis. In addition, reference may be made to books dealing specifically with analytical problems, such as Hamilton and Simpson, *Calculations of Analytical Chemistry,* McGraw-Hill, 1954.

THE SOLUTION OF MATHEMATICAL PROBLEMS

Often, for the solution of a mathematical problem several methods may be used to obtain the answer. In such cases, the question arises as to which one is preferable.

The ultimate goal in solving any problem is the correct answer. An individual who cannot achieve this end in practical work is a liability in any laboratory, no matter how elegant his method of operation may be. In contrast, anyone has a genuine advantage who can make calculations correctly, and at the same time secure the results quickly.

Perhaps each individual must decide what procedure is best for him to use in solving the problems encountered in analytical calculations. Thus, certain indirect problems, involving simultaneous equations, can be solved with or without the use of algebra. Several books are available that deal with the most common kinds of problems and with methods for solving them.[2] The subject is treated less comprehensively in various textbooks on quantitative analysis.

In connection with the explanation included herein for each type of illustrative problem, there is given first what seems a reasonably direct method of solution in most of the different sections. Along with this method there appears in many cases a factor-label or dimensional notation method. Because the latter approach is not widely used, a brief explanation is given below.

Factor-Label Method [3]

Experience has shown the need for a quick, logical, and reliable process of solving numerical problems in chemistry and related subjects of science and engineering. Use of the conventional proportion method, "This is to that as this is to that," does not meet this need for at least the following reasons: (1) it does not follow the reasoning process used in everyday thinking; (2) it indicates nothing about the units in which the answer is expressed; and (3) it may require considerable unnecessary work when more than one proportion is involved.

The factor-label method overcomes all these difficulties. It involves

[2] Arenson, *How To Solve Problems in Quantitative Analysis,* Crowell, 1938; Hamilton and Simpson, *Calculations of Analytical Chemistry,* McGraw-Hill, 1954; West, *Calculations of Quantitative Analysis,* Macmillan, 1948.

Although the author does not regularly use such a problem book, students who need additional drill are advised to work with such a text. In the different sections on succeeding pages, reference is made whenever possible to the text of Hamilton and Simpson because it is the most comprehensive of those listed. The fifth edition, 1954, is cited.

[3] The author is indebted to his colleague, Professor F. D. Martin, who furnished this material and checked the factor-label notations used in the examples in subsequent sections. See Martin, *Lecture Notebook and Questions,* John S. Swift and Co., 1948.

merely the use of simple conversion factors, properly labeled, such as 4 qts./gal., and 5280 ft./mi. To find the number of quarts in 10 gal., for example, the 10 gal. is multiplied by the factor 4 qts./gal. Stated mathematically this is

$$x \text{ qts.} = 10 \text{ gal.} \times \frac{4 \text{ qts.}}{1 \text{ gal.}} = 40 \text{ qts.}$$

This simple illustration follows three essential steps in using the factor-label method:

1. Set down an x, followed by the label that belongs to the answer.
2. Place an $=$ sign after the label and then give the quantities, each with its proper label, from which the problem is to be solved.
3. Multiply the *given* quantity by the *factor*, or series of factors, necessary to convert it into the *desired* quantity; that is, on canceling out labels, the remaining label on the right-hand side should be the label of the desired quantity on the left-hand side.

It should be noted that these factors are of such a nature that the numerator can always be set as equivalent to the denominator, and hence the factor may be inverted, if necessary. For example, since 4 qts. = 1 gal., it is equally correct to write 4 qts./1 gal. or 1 gal./4 qts., as each factor may be set equal to 1.

The following example illustrates the application of the method to a specific case.

If a sprinter runs 100 yds. in 10 sec., what was his speed in m.p.h.? In working this problem, the line of reasoning might be as follows:

(a) Note that the problem may be restated as an equation

$$x \text{ mi./hr.} = 100 \text{ yds./10 sec.}$$

(b) Since 1760 yds. = 1 mi., and 1 hr. = 3600 sec., the following unity factors are possible:

$$\frac{1760 \text{ yds.}}{1 \text{ mi.}} \quad \frac{1 \text{ mi.}}{1760 \text{ yds.}} \quad \frac{1 \text{ hr.}}{3600 \text{ sec.}} \quad \frac{3600 \text{ sec.}}{1 \text{ hr.}}$$

(c) Since *either* side of an equation may be multiplied by unity *any* number of times *without changing the equality,* the right-hand side of the equation in (a) is multiplied by a sufficient number of unity factors to convert yds./sec. to mi./hr.

(d) The correct factors are selected by choosing those that will result in the removal, by cancellation, of the *given* units and their replacement by the *desired* units. For the problem stated, the set-up would be

$$x \text{ mi./hr.} = \frac{100 \cancel{\text{yds.}}}{10 \cancel{\text{sec.}}} \times \frac{1 \text{ mi.}}{1760 \cancel{\text{yds.}}} \times \frac{3600 \cancel{\text{sec.}}}{1 \text{ hr.}}$$

$$= 20.4 \text{ mi./hr.}$$

Calculation Aids

The simple operations of arithmetic are the only mathematics required for dealing with the great majority of elementary analytical data. Whenever much calculating is necessary, the analyst should use some calculation aid.

To an engineer the most obvious device is his slide rule. However, the standard 10-in. rule will not suffice, if four significant figures are required. It is convenient for checking calculations made otherwise. A variety of rules and other devices having scales 20 in. or longer are available. The automatic electric calculating machine is the ultimate in gadgetry in this direction, of course.

Logarithm tables are probably most often used for this purpose. For the simplest work, not requiring many significant figures, the 4-place table may serve. Five-place tables generally are more useful. The author much prefers the graphic arrangement of logarithm figures, as prepared by LaCroix and Ragot.[4] The abbreviated form included in the Appendix reads directly to four places and the fifth may be estimated, just as with a slide rule. No proportional parts are involved, and one can go equally well from numbers to logs or the reverse. Little experience is needed.

SIGNIFICANT FIGURES [5]

The following problems illustrate the application of the principles and rules given in Chapter 22.

1. What sums should be reported for the following series of values: (a) 12.0981, 10.31, 24.374 g; (b) 20.1, 8.09, 13.392 ml; (c) 1.01891, 2.234, 6.5834 volts? *Ans.* (a) 46.78 g; (b) 41.6 ml; (c) 9.836 volts.

2. If the internal radius of a buret is 5.08 mm, what is the cross-sectional area? *Ans.* 81.0 sq. mm.

3. If 0.00120 g is used as the value for the mass of 1.00 ml of air, what weight is displaced on a balance by a cylinder 10.00 cm in diameter and 20.5 cm high? *Ans.* 1.93 g.

4. For the compounds represented by the following formulas calculate the formula weights to the maximum number of significant figures: (a) AgCl; (b) BH_3; (c) BeO; (d) H_2O; (e) H_2S; (f) H_2IrCl_6; (g) KF; (h) NaCl; (i) OsO_4; (j) S_2Cl_2. *Ans.* (a) 143.337; (b) 13.84; (c) 25.02; (d) 18.02; (e) 34.082; (f) 407.8; (g) 58.10; (h) 58.454; (i) 254.2; (j) 135.046.

5. If 0.02 ml is taken as a likely error in reading one position of the meniscus with a 50-ml buret, what is the error, in parts per 1000, for the following volumes: (a) 5.00; (b) 10.00; (c) 25.00; (d) 50.00 ml? *Ans.* (a) 4; (b) 2; (c) 0.8; (d) 0.4.

[4] *Graphic Table of Logarithms and Antilogarithms,* Macmillan, 1925.

[5] See Hamilton and Simpson, *op. cit.,* p. 5. See also Chapter 22 of this book.

6. In order to obtain a precision of 1 part per 1000, the samples indicated must be weighed to what amounts: (a) 5; (b) 1; (c) 0.5; (d) 0.2 g?

Ans. (a) ±0.005; (b) ±0.001; (c) ±0.0005; (d) ±0.0002 g.

EVALUATION OF A SERIES OF RESULTS[5]

Various approaches have been used to arrive at some measure of the precision of a series of successively determined values. The problems following illustrate several of these methods.

1. If one applies Rule 4 (page 363) in calculating the averages, what values should be reported for the following pairs of readings: (a) 22.979, 23.057; (b) 48.555, 48.717; (c) 73.61, 72.43; (d) 14.82, 14.68?

Ans. (a) 23.02; (b) 48.6; (c) 73; (d) 14.7 or 14.8.

2. Three determinations of the water of crystallization in barium chloride dihydrate gave the following percentages: 14.77, 14.81, 14.83. Based upon the theoretical percentage of water in this compound, what was the error of the determined average value, in per cent water, and its relative percentage error?

Ans. −0.05 per cent; 0.34 per cent.

3. The percentages found for iron in five samples of ore were 55.52, 55.69, 55.45, 55.65, 55.60. Calculate (a) the arithmetical mean; (b) the range of the deviation from the mean; (c) the average deviation from the mean; and (d) the standard deviation of the mean.

Ans. (a) 55.58; (b) +0.11 to −0.13; (c) 0.08; (d) 0.09 per cent.

4. The following values were obtained for the percentage of copper in brass: 75.80; 75.90; 75.78; 75.85; 75.76; 75.88; 75.83; 75.92; 75.81; 75.91. Calculate the average, the average deviation from the mean, and the standard deviation (σ).

Ans. Average 75.84; average deviation ±0.048; σ±0.054 per cent.

5. Evaluate the following series of triplicate readings according to the quality control scheme of Wernimont[6] and of Mitchell.[7] (See Chapter 22; treat the data in groups of three, as listed.)

8.56	8.55	8.48	8.54	8.42
8.39	8.49	8.53	8.49	8.52
8.46	8.50	8.45	8.53	8.48
8.55	8.54	8.51	8.43	8.44
8.51	8.44	8.50	8.53	8.47
8.49	8.46	8.48	8.50	8.56

DETERMINATION OF MASS VALUES (WEIGHTS)[8]

These problems deal with several aspects of weighing that need to be considered if really accurate work is required. The possible errors

[6] *Ind. Eng. Chem., Anal. Ed.* **18**, 587 (1946).

[7] *Anal. Chem.* **19**, 961 (1947).

[8] See Chapters 3 and 23 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 83.

involved may be neglected only in case their magnitude is insignificant in a given case. The items concerned here are the inequality of balance arms, and the buoyancy of the medium in which the weighing is made. In practically all cases this medium is air.

Balance errors may be determined or eliminated by double weighing, by use of the arm ratio, or by substitution weighing. There is always a buoyancy error except in the rare cases when the density of the object equals that of the weights. To calculate this error, one needs the densities of the object, the weights used, and the air under the conditions of weighing. Values for a few solids and for air are given in the Appendix.[9]

Example: On the basis of the values in the atomic weight table, it is calculated that 5.2995 g of Na_2CO_3 is needed for a given solution. If the material is weighed in air (30° and 750 mm) with tantalum weights, what apparent mass should be weighed? Neglect of the buoyancy would entail what percentage error?

Since the international atomic weights are based upon vacuum-weight masses, the calculated amount of sodium carbonate, for example, will not be correct for a weighing to be made in air with weights having a density differing from that of the carbonate.

The calculation of the buoyancy error involves the principle of Archimedes. The magnitude is the difference between the masses of air displaced by the object and by the weights. The expression relating the quantities involved is

$$M_v = M_a + (V_1 - V_2)m$$

in which,

M_v = mass of the object in a vacuum,
M_a = mass of the object in air,
V_1 = volume of the object,
V_2 = volume of the weights, and
m = mass of unit volume of air (density)

Expressing the equation in terms of volumes of object and of weights, we have

$$M_v = M_a + \left(\frac{M_v}{D_1} - \frac{M_a}{D_2}\right)m$$

D_1 and D_2 being, respectively, the densities of the object and of the weights. Since M_v (inside the parentheses) is unknown, M_a may be sub-

[9] Note that only variations in temperature and pressure are taken into account. In an actual, critical case, it might be necessary to determine the value in order to take into account other variables, e.g., humidity and content of carbon dioxide.

stituted for it. This is justified as the two values are nearly equal. The expression then becomes

$$M_v = M_a + \left(\frac{M_a}{D_1} - \frac{M_a}{D_2}\right) m$$

If M_a is desired, the expression is

$$M_a = M_v - \left(\frac{M_v}{D_1} - \frac{M_v}{D_2}\right) m$$

The required quantities are those involving the products of m and the several volumes M_a/D_1, . . .). The values of the densities may be found in the Appendix.

In the problem given, M_a is required, $M_v = 5.2995$, $D_{Na_2CO_3} = 2.53$, $D_{Ta} = 16.6$, and m (30° and 750 mm) = 0.00115. Then $(M_v/D_1)m = 0.0024$ g, and $(M_v/D_2)m = 0.0004$ g. The difference, or resultant correction, is 0.0020 g. The required air mass is then 5.2995 − 0.0020 = 5.2975 g. The percentage error, defined as the actual error/true value, multiplied by 100, is (0.0020/5.2975) × 100 = 0.038.

1. An object was weighed first on the left-hand pan and then on the right-hand pan of a given balance. If the respective values obtained were 25.4830 and 25.4880 g, calculate the true mass of the object, and the arm ratio of the balance. *Ans.* 25.4855 g; R/L = 1.0001.

2. In the calibration of a 20-g weight, it was placed on the right-hand pan of the balance. The weight balanced the counterpoise piece with the rider on the beam at 3.5 on the right-hand side. On replacing the weight being calibrated with the standard piece (19.9995 g), it was necessary to move the rider back to 2.0. Calculate the true mass of the unknown weight. *Ans.* 19.9980 g.

3. According to the atomic weight table, 10.0000 g of $KHC_8H_4O_4$ is needed for a given solution. If this amount is weighed in air (25° and 755 mm) against brass weights, what is the percentage error and its sign?

Ans. +0.057 per cent.

4. A vacuum weight of 20.0000 g of gold is needed. What weight should be taken, if the weighing is done in air (30° and 750 mm) with aluminum weights? Neglect of the buoyancy would involve what percentage error?

Ans. 20.0073 g; 0.037 per cent.

5. A tantalum vessel weighs 25.0000 g in air (30° and 740 mm) with silica weights. What would be the vacuum mass, and the percentage error?

Ans. 24.9911 g; 0.036 per cent.

6. A vacuum weight of 20.0000 g of sodium carbonate is needed. What weight should be taken, if the weighing is done in air (27° and 730 mm) with tantalum weights? Neglect of the buoyancy would involve what percentage error? *Ans.* 19.9925 g; 0.038 per cent.

7. An aluminum dish weighs 15.0000 g in air (15° and 760 mm) with

platinum weights. What would be the vacuum mass, and the percentage error? *Ans.* 15.0060 g; 0.040 per cent.

8. Diamonds are selling at \$200/carat (1 c = 0.2 g). A man pays \$400 for a stone which the jeweler said weighed 2 c. If the weighing was done in air (25° and 750 mm) with platinum weights, was the man over- or under-charged, and how much? *Ans.* Undercharged 11 cents.

9. Platinum scrap amounting to 50.0000 g was sold at \$300/g. If the weighing was done in air (20° and 730 mm) with silica weights, what was the seller's gain or loss, based on true mass value? *Ans.* Gain of 7 cents.

10. In an atomic weight determination the precipitate of silver chloride had an apparent mass of 3.75000 g. The weighing was done in air (20° and 740 mm). The gram pieces were brass, and the fractional pieces platinum. Calculate the true mass of the precipitate. *Ans.* 3.75031 g.

CALIBRATION OF VOLUMETRIC WARE [10]

For the kind of measurements covered in this book the calibration of ware to be used in titrimetric determinations (made by volume) consists in measuring (1) the mass of water contained in, or delivered by, vessels with a given graduation mark, or (2) the mass to be put into a vessel to establish a mark for a given volume. The former case is the more common.

The three corrections involved in calculating the true mass of the water are for density, buoyancy, and change in volume of the glass vessel with change in temperature. When the weighing is done under ordinary working conditions of temperature, most authors use the following expression to calculate the mass of water required for a true liter.

$$M_a = \frac{1000 \times D_1}{1 + \left(\frac{m}{D_1} \times \frac{m}{D_2}\right)} + [1000 \times D_1 \times c(t - 20)]$$

in which M_a = air-mass of water required for one liter, t = working temperature, D_1 = density of water at $t°$, D_2 = density of weights used, m = mass of 1 ml of air under the working conditions, and c = coefficient of cubical expansion of the glass vessel. Since memorization of such a formula is pedagogically questionable, the author prefers to calculate separately the three corrections concerned, as illustrated in the example given.

Example: Calculate the mass of water that should be weighed into a flask to fix a mark so that the vessel will hold exactly 1000 ml at 20°, the weighing to be done at 750 mm and 30°, in air, and with brass weights. Indicate the separate corrections for density, buoyancy, and expansion of glass, with the sign of each.

[10] See Chapters 4 and 24 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 141.

The *density* correction may be determined easily by reference to Table 4.7 (page 56). On the basis of the definition of the liter, 1000 g of water would be needed at 4°. Water expands above this temperature. At the specified temperature of 30° the mass to use is 1000 times the density at 30°, or 995.68 g (see column 2 of Table 4.7). The difference between this value and 1000 is 4.32 g. The correction is negative.

The *buoyancy* correction is a specific case of the general type discussed in the problems on weighing. The mass 995.68 g is a vacuum-weight value. $M_v = 995.68$, D_1 (water) $= 0.99568$, D_2 (weights) $= 8.0$, m (air at 30° and 750 mm) $= 0.00115$. Then $(M_v/D_1)m = 1.15$ g, and $(M_v/D_2)m = 0.14$ g. The difference, 1.01 g, is the buoyancy correction. As water is less dense than the weights, it is buoyed up more, and therefore weighs less than in a vacuum. Therefore, the correction is negative. The vacuum-weight minus the correction (995.68 — 1.01) gives 994.67 g, or the mass to take if the flask is to be used at 30°. If it is to be used at this temperature, there is no further calculation.

As the problem is to mark the flask at 30°, but to be correct at 20° (N.B.S. official temperature), there is an additional correction, for *expansion*. The flask holds slightly more at 30° than at 20°. To obtain the amount of the correction one uses the coefficient of cubical expansion, which is 0.000025 for the kind of glass employed. This is the change in volume/milliliter/degree. The product of this value times the volume changing (1000 ml) times the number of degrees change (10) gives 0.25 ml, or the change in volume of the flask. That is, it holds this much more at 30° than at 20°. Multiplying ml by 0.99568, the density of the water being weighed, gives 0.25 g as the mass to be used for the expansion correction. As the flask must hold more at 30° than at 20°, this amount is added to 994.67 to give 994.92 g, the answer to the problem. Although this correction is positive for temperatures above 20°, its sign reverses below 20°.

1. Calculate the mass of water to weigh into a flask to fix a mark so that the vessel will hold exactly 1200 ml at 20°, the weighing to be done in air (15° and 760 mm) with tantalum weights. Show the separate corrections and their signs. *Ans.* Density, −1.05 g; buoyancy, −1.38 g; contraction, −0.15 g; 1197.42 g needed.

2. Calculate the capacity at 20° of a pipet that delivers 24.950 g of water, the weighing being done in air (30° and 730 mm) with brass weights. Is the error within the N.B.S. tolerance (0.1 per cent of the volume concerned)? *Ans.* 25.09 ml; No.

3. Calculate the mass of water to weigh into a flask to fix a mark so that

the vessel will hold exactly 1500 ml at 20°, the weighing being done in air (27° and 750 mm) with platinum weights. Show the separate corrections and their signs. *Ans.* Density, −5.17 g; buoyancy, −1.66 g; expansion, +0.26 g; 1493.43 g needed.

4. Calculate the capacity at 20° of a vessel which delivers 30.00 g of mercury, the weighing being done in air (17° and 745 mm) with aluminum weights. *Ans.* 2.21 ml.

5. Calculate the mass of water to weigh into a flask to fix a mark so that the vessel will hold exactly 500 ml at 20°, the weighing being done in air (30° and 730 mm) with gold weights. Show the separate corrections and their signs. *Ans.* Density, −2.16 g; buoyancy, −0.53 g; expansion, +0.12 g; 497.43 g needed.

6. Calculate the average capacity/ml at 20° for the first 10-ml interval of a buret if the water delivered weighed 9.980 g, the weighing being done in air (15° and 755 mm) with brass weights. *Ans.* 1.000 ml.

7. A student filled his liter flask to the mark with water when the temperature was 35°. When he returned to the laboratory, the temperature was 18°. If the inside diameter of the neck of the flask was 15 mm, calculate the number of centimeters the meniscus would drop. *Ans.* 2.35 cm.

8. In a calibration made at 18° a student thought the barometric pressure was 720 mm and used 0.00115 as the density of air. Actually the pressure was 770 mm and the density of air 0.00123. Calculate the difference in the buoyancy correction for the water to be weighed for a liter flask with brass weights. *Ans.* 0.07 g.

AMOUNT OF A REAGENT REQUIRED [11]

The calculation of the amounts of many kinds of chemicals and industrial materials to be used for given transformations is a daily problem throughout chemical industry. One of the most important concepts in general chemistry is the reactivity of chemical species in terms of equivalent masses. Thus, according to the equation

$$C\ (12) + O_2\ (32) \rightarrow CO_2\ (44)$$

12 g of carbon react with 32 g of oxygen to give 44 g of carbon dioxide. Based upon this relationship of carbon and oxygen, one can multiply any weight of carbon by the factor 44/12 to obtain the corresponding weight of carbon dioxide. Such a ratio may be designated as a *conversion factor.*

This kind of reasoning is widely used in calculations involving the weight relationships expressed in chemical equations. Specific examples are the calculation of charges for operating a blast furnace, or for making mixes for a glass furnace.

The same method of calculation is involved often in analytical chemis-

[11] See Hamilton and Simpson, *op. cit.*, pages 27 and 100.

try, when one needs to know how much of a given reagent is required for a given purpose.

Example: How many milliliters of 4 per cent $(NH_4)_2C_2O_4$ solution sp. gr. 1.03 are needed to precipitate as CaC_2O_4 the calcium in 0.6000 g of limestone containing 85 per cent $CaCO_3$, if 5 per cent excess precipitant is used?

The chemical equations for the reactions involved are

$$CaCO_3 + 2\ HCl \rightarrow CaCl_2 + H_2O + CO_2\uparrow$$
$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4\downarrow + 2\ NH_4Cl$$

Therefore, 100.1 g of $CaCO_3 \simeq$ 124.1 g of $(NH_4)_2C_2O_4$.[12] As the sample of 0.6000 g contains only 85 per cent of $CaCO_3$, there is 0.5100 g of $CaCO_3$ to react. This weight times the ratio, $(NH_4)_2C_2O_4/CaCO_3$, gives the weight of pure oxalate needed. As the precipitant is a 4 per cent solution, 100/4 times the weight of pure salt gives the weight of solution. This weight divided by the sp. gr., 1.03, gives the volume of solution. As 5 per cent excess is to be provided, multiplication by 1.05 gives the volume required.

This type of problem illustrates the efficiency of the factor-label setup. Stated in this form,

$$x \text{ ml of soln.} = \frac{0.6000 \cancel{\text{ g sample}}}{1} \times \frac{85 \cancel{\text{ g } CaCO_3}}{100 \cancel{\text{ g sample}}} \times \frac{124.1 \cancel{\text{ g } (NH_4)_2C_2O_4}}{100.1 \cancel{\text{ g } CaCO_3}} \times$$
$$\frac{100 \cancel{\text{ g soln.}}}{4 \cancel{\text{ g } (NH_4)_2C_2O_4}} \times \frac{100.1 \text{ ml soln.}}{1.03 \text{ g soln.}} \times \frac{(100 + 5)}{100}$$
$$= 16.1 \text{ ml soln.}$$

1. A sample of 2.750 g of Cu is dissolved in HNO_3, according to the equation

$$3\ Cu + 8\ HNO_3 \rightarrow 3\ Cu(NO_3)_2 + 2\ NO\uparrow + 4\ H_2O$$

Calculate (a) the weight of $Cu(NO_3)_2$ formed, (b) the volume of 67 per cent HNO_3 (sp. gr. = 1.40) necessary, and (c) the weight of CuO that would be obtained on evaporation of the solution and ignition of the residue.

Ans. (a) 8.117 g; (b) 7.75 ml; (c) 3.442 g.

2. Calculate the volume of a solution of 36 per cent HCl (sp. gr. = 1.183) required to make 10 liters of 6 *M* solution. *Ans.* 5137 ml.

3. A sample of 0.4000 g contains 12.5 per cent of sulfur. Calculate the volume of 5 per cent solution of $BaCl_2 \cdot 2\ H_2O$ (sp. gr. = 1.05) required to form the precipitate of $BaSO_4$, assuming the use of 2 per cent excess of precipitant. *Ans.* 7.40 ml.

[12] All numerical values for the problems in this chapter were calculated with the atomic weights of 1949. Consequently, very small discrepancies will be found if the 1953 values are used for aluminum, iodine, phosphorus, potassium, and silicon. A list of formula weights used in the problems is included at the end of this chapter.

4. If 7.5 ml of a 1.5 per cent HCl solution (sp. gr. = 1.037) is used to precipitate silver as AgCl from a sample of 0.8000 g, what will be the maximum percentage of silver that can be handled? *Ans.* 43.1 per cent.

5. The CO_2 is liberated from 0.5000 g samples of limestone, containing 90 per cent $CaCO_3$, by means of 10 per cent $HClO_4$ (sp. gr. = 1.060). What volume of acid is needed, if 5 per cent excess is provided? Under standard conditions, what volume of CO_2 would be evolved?

Ans. 8.95 ml $HClO_4$; 100.7 ml CO_2.

6. Assume that the CO_2 evolved in Problem 5 is absorbed in 30 per cent KOH solution (sp. gr. = 1.290) with the formation of K_2CO_3. If the absorption bulb holds 15 ml of absorbent, what is the maximum number of samples that can be run and leave a safety factor of 10 per cent of KOH unused? *Ans.* 10 samples.

7. How many pounds of 48 per cent H_2SO_4 solution will be required to neutralize a ton of Na_2CO_3, $NaHCO_3$, and $CaCO_3$?

Ans. 3855 lbs. Na_2CO_3; 2432 lbs. $NaHCO_3$; 4083 lbs. $CaCO_3$.

8. Which is the cheaper source of CO_2, $CaCO_3$ at 0.25 cents/lb. or Na_2CO_3 1.5 cents/lb.? How much? *Ans.* $CaCO_3$; 6.35 times.

NEUTRALIZATION METHODS [13]

A considerable number of problems are included here to illustrate the use of acids and alkalies in titrimetry. The problems have been subdivided into several types to emphasize certain calculative details. In general, the sequence is that encountered in preparing and using such solutions in practical work.

1. Equivalent Weights

Although the usually stated merits of the normal system of specifying concentration of titrants is open to serious question,[14] most chemists are thoroughly conditioned to thinking in these terms. If one uses the system, equivalent weights are involved, as a normal solution contains one gram-equivalent weight of solute per liter of solution. An equivalent weight is the mass of solute that reacts with, or is chemically equivalent to, 8.000 g of oxygen or 1.0080 g of hydrogen (or 17.008 g of OH^- ions for alkalies). Some analysts prefer to work in terms of milliequivalent weights, or milliequivalents.

The problem, then, with acids and alkalies is to decide on the fraction of the gram-molecular weight to use for the compound in question. This is determined from the number of H^+ or OH^- ions with which the substance *reacts* according to the equation involved. It should be noted that

[13] See Chapters 12, 13, and 25 for a general discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 145.

[14] See Mellon, *J. Chem. Educ.* 17, 422 (1940).

this number may or may not be the total number of such ions per molecule. Thus, it was mentioned in Chapter 12 that phosphoric acid, H_3PO_4, theoretically has three equivalent weights, depending upon whether one, two, or three of the hydrogens react. Practically, there are only two cases for direct titrations, for with methyl orange as the indicator one hydrogen reacts and with phenolphthalein as the indicator two react. Another common example is sodium carbonate, Na_2CO_3. If methyl orange is used as the indicator, the reaction is

$$2\ H^+ + CO_3^{-2} \rightarrow H_2O + CO_2\uparrow$$

and if phenolphthalein is used, the equation is

$$H^+ + CO_3^{-2} \rightarrow HCO_3^-$$

Obviously, the equivalent weight may be a variable quantity. The chemical equation for the reaction must be known for any given case.

Often one wants to calculate in terms of some atom or group of atoms. Thus, for the reaction

$$Ca(OH)_2 + H_3PO_4 \rightarrow CaHPO_4 + 2\ H_2O$$

what is the equivalent weight of phosphorus, and also of phosphorus pentoxide, P_2O_5? As two hydrogen (or hydroxyl) ions react, the milliequivalent weight is 1/2000 of the atomic weight of phosphorus, or 31.04/2000. For the P_2O_5 value, one may consider the above equation as multiplied by two, in order to get two phosphorus atoms. Then the molecular weight of P_2O_5 divided by 4 is the equivalent weight, because four OH^- ions are involved.

To illustrate such cases further, calculate the equivalent weights of the compounds or elements indicated by boldface type in the following equations (or the constituents in the parentheses at the end):

1. $2\ \mathbf{HCl} + Ba(OH)_2 \rightarrow BaCl_2 + 2\ H_2O$
2. $2\ \mathbf{NH_4OH} + H_2SO_4 \rightarrow (NH_4)_2SO_4 + 2\ H_2O$ **(N_2O_5)**
3. $\mathbf{Na_2CO_3} + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2\uparrow$ **(C)**
4. $\mathbf{Na_2CO_3} + HCl \rightarrow NaHCO_3 + NaCl$ **(Na_2O)**
5. $\mathbf{H_3PO_4} + KOH \rightarrow KH_2PO_4 + H_2O$ **(P)**
6. $\mathbf{Ca(OH)_2} + H_2C_2O_4 \rightarrow CaC_2O_4 + 2\ H_2O$ **(CaO)**
7. $\mathbf{H_3PO_4} + 2\ LiOH \rightarrow Li_2HPO_4 + 2\ H_2O$ **(P_2O_5)**
8. $2\ \mathbf{NaHCO_3} + H_2SO_4 \rightarrow Na_2SO_4 + 2\ CO_2\uparrow + 2\ H_2O$
9. $\mathbf{H_3PO_4} + 3\ NaOH \rightarrow Na_3PO_4 + 3\ H_2O$
10. $\mathbf{Na_2B_4O_7} + 2\ HClO_4 \rightarrow H_2B_4O_7 + 2\ NaClO_4$
11. $2\ \mathbf{KHC_8H_4O_4} + Ba(OH)_2 \rightarrow BaC_8H_4O_4 + 2\ H_2O + K_2C_8H_4O_4$
12. $\mathbf{H_2CO_3} + Ba(OH)_2 \rightarrow BaCO_3 + 2\ H_2O$ **(CO_2)**
13. $\mathbf{H_2SiF_6} + 6\ KOH \rightarrow 6\ KF + SiO_2 + 4\ H_2O$

14. $C_3H_5OH \cdot BO_3H + NaOH \rightarrow C_3H_5OH \cdot BO_3Na + H_2O$ **(B_2O_3)**
15. $2\ (NH_4)_3\ [P(Mo_3O_{10})_4] + 46\ NaOH \rightarrow 2\ (NH_4)_2HPO_4 + (NH_4)_2MoO_4 + 23\ Na_2MoO_4 + 22\ H_2O$ **(P_2O_5)**

2. *Preparation of Solutions*[15]

The general problem in the preparation of solutions is to calculate the amount of a substance needed to prepare a given amount (usually volume) of a solution of a specified value. If the material is a primary standard, such as potassium hydrogen phthalate or constant-boiling-point hydrochloric acid, the calculated mass may be weighed, transferred to a flask, and diluted to volume. Otherwise, the solution is made to the approximate value desired and then standardized. In the latter case, if dilution is to be made to an exact value following standardization, the initial solution is made slightly more concentrated than that desired.

There is some choice in the system used to express the value of the solution. In general, it will be in terms of (1) the titrant itself, or (2) something with which unit amount of titrant will react, or to which it is chemically equivalent. If it is in terms of the titrant, the common specifications are (1) concentration of solute, in grams, per milliliter of solution, (b) normality, (3) molarity, or (4) some over-all mass basis, such as molality. The last practice is uncommon.

Example 1: How many grams of Na_2CO_3 should be taken for (a) 250 ml of 0.2000 *N* solution, and (b) 500 ml of a solution the HCl titer of which is 0.004000 g?

(a) To solve this part of the problem it will be assumed that the reaction of the carbonate with an acid is complete, as represented by the equation

$$Na_2CO_3\ (106.00) + 2\ HCl\ (36.46) \rightarrow 2\ NaCl + H_2O + CO_2\uparrow$$

Therefore, the gram molecular weight of $Na_2CO_3/2$ is the equivalent weight, or the amount for 1 liter of 1.0000 *N* solution. As the volume is to be 0.25 liter and the normality is to be 0.2, we may write

$$\frac{106.00}{2} \times \frac{25}{100} \times \frac{2}{10} = 2.650\ \text{g}\ Na_2CO_3$$

Or, in factor-label form

$$x\ \text{g}\ Na_2CO_3 = 0.25 \cancel{\text{ l soln.}} \times \frac{0.2 \cancel{\text{ g eq. wt.}}}{1 \cancel{\text{ l soln.}}} \times \frac{106.00\ \text{g}\ Na_2CO_3}{2 \cancel{\text{ g eq. wt.}}}$$

$$= 2.650\ \text{g}\ Na_2CO_3$$

(b) As the HCl titer is to be 0.004000 g, each milliliter of titrant will have to contain an equivalent amount of Na_2CO_3. This desired value is

[15] See Hamilton and Simpson, *op. cit.*, p. 145.

the titer value multiplied by the ratio $Na_2CO_3/2$ HCl. Multiplying the product by 500 gives the total amount. Stated in factor-label form, we have

$$x \text{ g } Na_2CO_3 = 500 \text{ ml soln.} \times \frac{0.004000 \text{ g HCl}}{1 \text{ ml soln.}} \times \frac{106.00 \text{ g } Na_2CO_3}{2(36.46) \text{ g HCl}}$$

$$= 2.907 \text{ g } Na_2CO_3$$

Example 2: How many milliliters of a solution of H_2SO_4 (20 per cent H_2SO_4 and sp. gr. 1.140) should be taken for 2 liters of a solution (a) to be 0.2000 *N*, (b) each milliliter of which is equivalent to 0.001500 g of nitrogen, and (c) each milliliter contains 0.005000 g H_2SO_4? Allow 5 per cent excess so that the solution may be standardized and then diluted to the desired value.

It will be assumed that the acid is to be used for complete neutralizations. The relationship involving nitrogen is shown by the equation

$$H_2SO_4 + 2\ NH_4OH \rightarrow (NH_4)_2SO_4 + 2\ H_2O$$

Hence, $H_2SO_4/2$, $\approx$ N; or 98.08/2 g $H_2SO_4 \approx$ 14.01 g N. In order to simplify the factor cancellations, rounded off values of 49 and 14 will be used.

(a) As the equivalent weight of the acid is 49, 1 liter of 1.000 *N* solution would require this amount in grams. For the 0.2000 *N* solution, 1/5 of this amount is needed. Multiplying by 2 gives the amount of pure H_2SO_4 for 2 liters. As the stock solution contains only 20 per cent H_2SO_4, it is necessary to multiply by 5 to obtain the grams of 20 per cent solution. Then, because each milliliter weighs 1.14 g, dividing the total mass by the sp. gr. 1.14 gives the total volume in ml. Finally, 105 per cent of this volume provides the 5 per cent excess.

This type of problem is an excellent example of the efficiency of working by setting down the necessary multiplying factors. Specifically, the above steps in reasoning are represented by the setup

$$\frac{98}{2} \times \frac{1}{5} \times \frac{2}{1} \times \frac{100}{20} \times \frac{1}{1.14} \times \frac{105}{100} = 85.9 \text{ ml of soln. I}$$

After cancellation, one multiplication and one division remain. If labels are used, we have

$$x \text{ ml soln. I} = 2 \text{ l soln. II} \times \frac{0.2 \text{ g eq. } H_2SO_4}{1 \text{ l soln. II}} \times \frac{98 \text{ g } H_2SO_4}{2 \text{ g eq. } H_2SO_4} \times \frac{100 \text{ g soln. I}}{20 \text{ g } H_2SO_4} \times \frac{1 \text{ ml soln. I}}{1.14 \text{ g soln. I}} \times \frac{(100 + 5)\ \%}{100\ \%}$$

$$= 85.9 \text{ ml soln. I}$$

(b) If each milliliter of acid is to be equivalent to 0.001500 g of nitrogen, the acid content per milliliter must be $0.001500 \times 49/14$. Multiplying the product by 2000 gives the mass required for 2 liters. One milliliter contains 20 per cent of 1.14 g of H_2SO_4, or 0.228 g. Dividing the total mass required by this mass/ml gives the required volume of stock solution. Again, 105 per cent of this volume provides for the required excess. Stated in factor form

$$\frac{0.001500}{1} \times \frac{49}{14} \times \frac{2000}{1} \times \frac{1}{1.14} \times \frac{100}{20} \times \frac{105}{100} = 48.4 \text{ ml soln. I}$$

Labeling the quantities gives

$$x \text{ ml soln. I} = 2000 \cancel{\text{ml soln. II}} \times \frac{0.001500 \cancel{\text{g N}}}{1 \cancel{\text{ml soln. II}}} \times \frac{49.04 \cancel{\text{g } H_2SO_4}}{14.01 \cancel{\text{g N}}} \times \frac{100 \cancel{\text{g soln. I}}}{20 \cancel{\text{g } H_2SO_4}} \times \frac{1 \text{ ml soln. I}}{1.14 \cancel{\text{g soln. I}}} \times \frac{(100 + 5) \cancel{\%}}{100 \cancel{\%}}$$

$$= 48.4 \text{ ml soln. I}$$

(c) If each milliliter is to contain 0.005000 g of H_2SO_4, the total acid required for 2 liters will be 2000×0.005000. As in (b), each milliliter of stock solution contains 20 per cent of 1.14 g, or 0.228 g. Dividing the total mass required by the mass/ml gives the required volume of stock solution, and multiplying by 1.05 provides the required excess. Stated in factor form

$$\frac{0.005000}{1} \times \frac{2000}{1} \times \frac{1}{1.14} \times \frac{100}{20} \times \frac{105}{100} = 46.0 \text{ ml soln. I}$$

Labeling the quantities gives

$$x \text{ ml soln. I} = 2000 \cancel{\text{ml soln. II}} \times \frac{0.005000 \cancel{\text{g } H_2SO_4}}{1 \cancel{\text{ml soln. II}}} \times \frac{100 \cancel{\text{g soln. I}}}{20 \cancel{\text{g } H_2SO_4}} \times \frac{1 \text{ ml soln. I}}{1.14 \cancel{\text{g soln. I}}} \times \frac{(100 + 5) \cancel{\%}}{100 \cancel{\%}}$$

$$= 46.0 \text{ ml soln. I}$$

1. How many milliliters of HCl solution (30 per cent HCl and sp. gr. 1.15) should be diluted to 2.5 liters to make (a) the solution 0.1 *M*, (b) the concentration 0.004000 g HCl/ml, and (c) each milliliter equivalent to 0.003000 g of Na_2O? *Ans.* (a) 26.4 ml; (b) 29.0 ml; (c) 25.6 ml.

2. Calculate the weight of NaOH required for 2 liters of a solution (a) 0.1500 *N*, (b) each milliliter of which is equivalent to 0.003500 g of B_2O_3 (see equation 14), and (c) each milliliter of which contains 0.005000 g NaOH. *Ans.* (a) 12.00 g; (b) 8.04 g; (c) 10.00 g.

3. How many milliliters of H_2SO_4 solution (40 per cent H_2SO_4 and sp. gr. 1.25) should be diluted to 5 liters to make (a) each milliliter equivalent to

0.002000 g of nitrogen (see equation 2), (b) the concentration 0.006000 g of H_2SO_4/ml; and (c) the solution 0.2000 *N*?

Ans. (a) 70.0 ml; (b) 60.0 ml; (c) 98.1 ml.

4. Calculate the weight of Na_2CO_3 required for 2.5 liters of a solution (a) 0.2000 *N*, (b) each milliliter of which is equivalent to 0.005000 g of H_2SO_4, and (c) each milliliter contains 0.003000 g of Na_2CO_3 (see equation 3).

Ans. (a) 26.50 g; (b) 13.51 g; (c) 7.500 g.

5. How many milliliters of HCl solution (37 per cent HCl and sp. gr. 1.18) should be diluted to 2 liters to make (a) the normality 0.2000, (b) the concentration 0.003500 g HCl/ml, and (c) the titer = 0.004000 g in terms of Na_2O (see equation 4)? Allow 5 per cent excess in each case to provide for dilution after standardization. *Ans.* (a) 35.1 ml; (b) 16.8 ml; (c) 22.6 ml.

6. Calculate the weight of $Ba(OH)_2 \cdot 8\ H_2O$ required for 2.5 liters of a solution (a) having a titer of 0.0005000 g in terms of carbon (see equation 12), (b) each milliliter of which contains 0.01000 g of barium, and (c) which is 0.1500 *N*. *Ans.* (a) 32.83 g; (b) 57.42 g; (c) 59.16 g.

7. Calculate the weight of constant-boiling-point HCl solution,[16] distilled at 750 mm, for 2 liters of a solution that has a titer of 0.005000 g in terms of Na_2CO_3 (see equation 3). *Ans.* 33.95 g.

8. Calculate the weight of constant-boiling-point HCl solution, distilled at 730 mm, for 5 liters of a solution that is to be exactly 0.1000 *N*.

Ans. 89.78 g.

9. Calculate the milliequivalent weight of phosphorus (see equation 15). How many grams of NaOH would be required for 1500 ml of a solution, each milliliter of which is equivalent to 0.0004000 g of P?

Ans. 0.001347 g; 17.82 g.

10. Calculate the milliequivalent weight of silicon (see equation 13). How many grams of KOH would be required to prepare 2 liters of a solution having a Si titer of 0.001000 g? *Ans.* 0.004677 g; 23.99 g.

3. *Standardization of Solutions*[17]

One must know the reacting value of a titrant in order to calculate the amount of a desired constituent from the amount of the standard solution used in a titration. The common methods employed to determine the value of a titrant may be illustrated for a solution of hydrochloric acid. The value is usually expressed in terms of grams per milliliter (occasionally g/g of solution), normality, molarity, or titer (equivalency).

Direct weighing of material. This method has been covered in the preceding section under the preparation of solutions. Use of constant-boiling-point hydrochloric acid is the specific example.

In general, this procedure is preferable, as it involves only weighing,

[16] See Table 25.1, page 401.

[17] See Hamilton and Simpson, *op. cit.*, p. 153.

transferring, and diluting the material. The weighing error can be minimized to almost any desirable point by taking sufficient solute. Material of requisite purity is assumed.

Standardization of the solution. If the purity of the material is not known to a degree to warrant direct weighing, the solution is made to the approximate concentration desired and then standardized. Two methods of standardization are widely used.

Comparison of the solution with a standard. To determine the chemical reactivity of a titrant by comparison with a standard two modifications are commonly used: (1) the amount of titrant equivalent to a weighed amount of a solid standard is determined; or (2) the amount of titrant reacting with a previously standardized solution is determined.

Use of a weighed amount of a solid standard needs no explanation beyond the statement of the following example.

Example: A mass of 0.3600 g of Na_2CO_3 reacts with 30.00 ml of HCl solution. Calculate for the acid (a) its concentration, in g HCl/ml, (b) its normality, and (c) its Na_2O titer.

(a) The equation for the reaction is

$$2\ HCl + Na_2CO_3 \rightarrow 2\ NaCl + H_2O + CO_2\uparrow$$
$$2\ HCl \eqsim Na_2CO_3 \eqsim Na_2O$$

from which

$$2(36.46) \eqsim 106.00 \eqsim 62.00$$

Dividing the 0.3600 g of Na_2CO_3 by the 30.00 ml reacting with it gives directly the Na_2CO_3 titer. As 2 HCl $\eqsim$ Na_2CO_3, multiplying this titer by the factor 2 HCl/Na_2CO_3 gives the concentration of HCl in g/ml. Stated in factor-label form

$$x\ \text{g HCl/ml HCl soln.} = \frac{0.3600\ \cancel{\text{g } Na_2CO_3}}{30.00\ \text{ml HCl soln.}} \times \frac{2(36.46)\ \text{g HCl}}{106.00\ \cancel{\text{g } Na_2CO_3}}$$
$$= 0.008255\ \text{g HCl/ml HCl soln.}$$

(b) Two simple calculations of the required normality are given. The answer in (a), 0.008255 g, is the actual g HCl/ml. If the solution were normal, this value would be 36.46/1000, or 0.03646 g. Therefore, the actual concentration divided by the concentration for a normal solution gives the normality, 0.2264 *N*.

Or one may start with the original data and calculate the Na_2CO_3 titer, as in (a). Then, a normal solution would have as its Na_2CO_3 titer 106.00/2000, or 0.05300 g. Therefore, the actual titer divided by the

titer for a normal solution gives the normality. Stated in factor-label form

$$x\,N = \frac{\text{meq. HCl}}{\text{1 ml HCl soln.}} = \frac{0.3600\ \text{g } Na_2CO_3}{30.00\ \text{ml HCl soln.}} \times \frac{\text{1 meq. HCl}}{0.05300\ \text{g } Na_2CO_3}$$

$$= 0.2264\ N$$

(c) This part of the problem illustrates the important item of calculating from one titer to another. Actually, the transformation involves only multiplying the given titer by the factor, eq. wt. of desired constituent/eq.wt. of known constituent. Equivalent formula weights are equally applicable, of course.

As in (a), dividing 0.3600 g of Na_2CO_3 by the 30.00 ml of HCl solution gives the titer in terms of Na_2CO_3.[18] From the equation given above, the multiplying factor required is Na_2O/Na_2CO_3. Stated in factor-label form

$$x\,T_{Na_2CO_3} = \text{g } Na_2O\text{/ml HCl soln.}$$

$$= \frac{0.3600\ \text{g } Na_2CO_3}{30.00\ \text{ml HCl soln.}} \times \frac{62.00\ \text{g } Na_2O}{106.00\ \text{g } Na_2CO_3}$$

$$= 0.007019\ \text{g } Na_2O\text{/ml HCl soln.}$$

In the standardization of a titrant through reaction with a previously standardized solution, usually a given volume of the unknown solution may be titrated with the standard solution, or vice versa. The value of the standard solution may be known, of course, in terms of concentration (grams/unit amount), normality, molarity, or titer. The required value for the unknown solution must be calculated accordingly. Three such possibilities are illustrated in the example.

Example: A volume of 40.00 ml of HCl solution reacted with 30.00 ml of NaOH solution. Calculate (a) the normality of the acid if the concentration of the NaOH is 0.005000 g/ml; (b) the concentration of the acid in g/ml if the NaOH titer in terms of H_2SO_4 is 0.006000 g; and (c) the titer of the acid in terms of nitrogen if the NaOH is 0.1200 *N*.

The equation for the standardization reaction is

$$HCl + NaOH \rightarrow NaCl + H_2O$$

For the separate parts of the problem the relationships needed are

HCl	$\Leftrightarrow$	NaOH	$\Leftrightarrow$	$H_2SO_4/2$	$\Leftrightarrow$	N
36.46		40.00		49.09		14.01

(a) Dividing the concentration of the NaOH, 0.005000 g/ml, by the milliequivalent weight, 0.04000 g, gives the normality of the NaOH solu-

[18] The expression $T_{Na_2CO_3}$ is used for the titer in terms of sodium carbonate.

tion. As the normalities of such reacting pairs are inversely proportional to the equivalent volumes, multiplying the normality of the NaOH solution by 30/40 gives the normality of the acid.[19] Stated in factor-label form

$$x\,N = \frac{\text{meq. HCl}}{1\text{ ml HCl soln.}}$$

$$= \frac{30.00\ \cancel{\text{ml NaOH soln.}}}{40.00\text{ ml HCl soln.}} \times \frac{1\text{ meq. HCl}}{0.04000\ \cancel{\text{g NaOH}}} \times \frac{0.005000\ \cancel{\text{g NaOH}}}{1\ \cancel{\text{ml NaOH soln.}}}$$

$$= 0.09375\ N$$

(b) The concentration of the NaOH solution in g/ml will be 0.006000 multiplied by the reacting ratio of the equivalent masses of NaOH and H_2SO_4, or 40.00/49.04. Then this value times the ratio of the equivalent masses of HCl and NaOH, or 36.46/40.00, gives the concentration which the milliliter of HCl would have if the acid and alkali reacted milliliter for milliliter. As 40.00 ml of acid reacts with 30.00 ml of alkali, the calculated value must still be multiplied by the ratio 30/40. Stated in factor-label form

$$x\text{ g HCl/ml HCl soln.} = \frac{30.00\ \cancel{\text{ml NaOH soln.}}}{40.00\text{ ml HCl soln.}} \times \frac{0.006000\ \cancel{\text{g } H_2SO_4}}{1\ \cancel{\text{ml NaOH soln.}}} \times$$

$$\frac{40.00\ \cancel{\text{g NaOH}}}{49.04\ \cancel{\text{g } H_2SO_4}} \times \frac{36.46\text{ g HCl}}{40.00\ \cancel{\text{g NaOH}}}$$

$$= 0.005444\text{ g HCl/ml HCl soln.}$$

Although the reasoning has been stated in two steps, inspection of the factors for reacting ratios shows that one should go directly by using only the ratio of the reacting masses of HCl and H_2SO_4, or 36.46/49.04.

(c) If the NaOH and HCl solutions had the same reactivity, milliliter for milliliter, the titer of the NaOH, in terms of HCl, would be 0.03646 × 0.1200, or 0.004375 g. Multiplying this value by the ratio of the reacting volumes, 30/40, gives the actual $T_{(HCl)}$. As indicated in connection with the problem, N ≑ HCl. Therefore, multiplying the $T_{(HCl)}$ by the ratio N/HCl gives the $T_{(N)}$. Stated in factor-label form

[19] This is an application of the much-taught relationship, $V_1N_1 = V_2N_2$. It implies that 1 ml of a 1 *N* solution always equals 1 ml of another 1 *N* solution. This is not necessarily true, for example, if normalities obtained with indicators of different pK_a values are compared; thus, the mass of orthophosphoric acid present per milliliter of 1 *N* solution is different when titrating with methyl orange or phenolphthalein as indicators. In general, normality applies only to a specified reaction; the equivalent weight of phosphoric acid and the normality of a phosphoric acid solution depend upon the indicator used, whereas those with hydrochloric acid do not.

$$x\ T_N = \text{g N/ml HCl soln.}$$

$$= \frac{30.00\ \text{ml NaOH soln.}}{40.00\ \text{ml HCl soln.}} \times \frac{0.03646\ \text{g HCl}}{1\ \text{meq. NaOH}} \times \frac{0.1200\ \text{meq. NaOH}}{1\ \text{ml NaOH soln.}} \times \frac{14.01\ \text{g N}}{36.46\ \text{g HCl}}$$

$$= 0.001261\ \text{g N/ml HCl soln.}$$

Gravimetric determination of a constituent separated from the solution. Three variations of the gravimetric procedure for the determination of a constituent separated from the solution are in common use. They all involve the use of a measured volume (or mass) of the solution. In some cases, such as a solution of sodium chloride, evaporation to dryness yields a product that may be weighed. In some an ion may be separated by electrodeposition, as Ag^+ ion from a solution of silver nitrate (complexed with cyanide), and weighed as the metal. In most cases a compound is formed by precipitation, removed, and weighed. Only the last type is a possibility for hydrochloric acid. In this case the preferable compound for weighing is the chloride, AgCl.

Example: A volume of 40.00 ml of HCl solution yields a precipitate of AgCl weighing 0.8000 g. Calculate the normality of the acid.

The equation for the reaction is

$$HCl + AgNO_3 \rightarrow AgCl\downarrow + HNO_3$$

from which $36.46 \quad \Rightarrow \quad 143.34$

Dividing the weight of AgCl, 0.8000 g, by the volume of acid yielding the precipitate, 40.00 ml, gives the $T_{(AgCl)}$. Multiplying this titer by the ratio of equivalent masses of HCl and AgCl, 36.46/143.34, gives the g HCl/ml. If the acid were normal, this value would be 0.03646. Therefore, dividing the determined g/ml by that of a normal solution gives the normality, 0.1395 *N*. Stated in factor-label form

$$x\ N = \frac{\text{meq. HCl}}{\text{1ml HCl soln.}}$$

$$= \frac{0.8000\ \text{g AgCl}}{40.00\ \text{ml HCl soln.}} \times \frac{36.46\ \text{g HCl}}{143.34\ \text{g AgCl}} \times \frac{1\ \text{meq. HCl}}{0.03646\ \text{g HCl}}$$

$$= 0.1395\ N$$

Other specification values for the acid may be calculated easily.

1. If 3.500 g of Na_2CO_3 are dissolved and diluted to 500 ml, calculate (a) the normality of the solution, (b) its $T_{(H_2SO_4)}$, and (c) the volume of 0.1000 *N* HCl with which 30.00 ml of the carbonate solution would react.

Ans. (a) 0.1321 *N*; (b) 0.006478 g; (c) 39.63 ml.

2. What is the titer of a 0.0950 N KOH solution in terms of C, Si, B, and P (see equations 12 to 15, page 621).

Ans. 0.0005705 g C; 0.0004443 g Si; 0.001028 g B; 0.0001280 g P.

3. If 10.530 g of constant-boiling-point HCl solution, distilled at 745 mm, is diluted to 500 ml, calculate (a) the g HCl/ml, (b) the normality, and (c) the titers in terms of BaO and N (see Table 25.1, page 401).

Ans. (a) 0.004269 g; (b) 0.1171 N;
(c) 0.008979 g BaO and 0.001640 g N.

4. If 30.00 ml. of KOH solution $\simeq$ 0.5000 g $H_2C_2O_4 \cdot 2\ H_2O$, calculate (a) the molarity of the solution, (b) its concentration in g/ml, and (c) the titer in terms of N_2O_5 (the anhydride of HNO_3).

Ans. (a) 0.2644 M; (b) 0.01483 g; (c) 0.01428 g.

5. If 25.00 ml of HCl solution react with 0.4000 g of Na_2CO_3, calculate the acid's (a) normality, (b) concentration in g/ml, and (c) titer in terms of CaO. *Ans.* (a) 0.3019 N; (b) 0.01101 g; (c) 0.008465 g.

6. If 35.00 ml of $Ba(OH)_2$ solution $\simeq$ 1.0500 g $KHC_8H_4O_4$, calculate the alkali's (a) molarity, (b) concentration in g/ml, and (c) carbon dioxide titer.

Ans. (a) 0.07345 M; (b) 0.01259 g; (c) 0.003233 g.

7. If 30.00 ml of NaOH solution react with 0.9000 g of sulfamic acid (one replaceable hydrogen in $HOSO_2NH_2$), calculate for the NaOH the (a) normality, (b) concentration in g/ml, and (c) the titer in terms of B_2O_3.

Ans. (a) 0.3089 N; (b) 0.01236 g; (c) 0.01076 g.

8. If 25.00 ml of a $Ba(OH)_2$ solution $\simeq$ 30.00 ml of 0.06000 M H_2SO_4 solution, calculate (a) the normality of the alkali solution, (b) its concentration in g/ml, and (c) the $T_{(CO_2)}$.

Ans. (a) 0.1440 N; (b) 0.01234 g; (c) 0.003169 g.

9. If 30.00 ml of HCl solution $\simeq$ 25.00 ml of a solution containing 3.000 g of Na_2CO_3/250 ml, calculate (a) g HCl/ml, (b) the normality of the acid, and (c) its $T_{(K_2O)}$. *Ans.* (a) 0.006880 g; (b) 0.1887 N; (c) 0.008887 g.

10. If 25.00 ml of NaOH solution $\simeq$ 24.00 ml of a solution of H_2SO_4 the $T_{(N)}$ of which is 0.001500 g, calculate the alkali's (a) molarity, (b) concentration in g/ml, and (c) potassium hydrogen phthalate titer.

Ans. (a) 0.1028 M; (b) 0.004112 g; (c) 0.02099 g.

11. If 25.00 ml of a solution of H_2SO_4 gave a precipitate of $BaSO_4$ weighing 0.7500 g, calculate the acid's (a) normality, (b) concentration in g/ml, and (c) K_2CO_3 titer. *Ans.* (a) 0.2571 N; (b) 0.01261 g; (c) 0.01777 g.

12. If 30.00 ml of HCl solution gave a precipitate of 0.6600 g of AgCl, calculate the acid's (a) concentration in g/ml, (b) molarity, and (c) titer in terms of carbon (2 HCl $\simeq$ H_2CO_3).

Ans. (a) 0.005597 g; (b) 0.1535 M; (c) 0.0009218 g.

13. A solution of 20.00 ml of H_2SO_4 was neutralized with 22.00 ml of NaOH solution. On evaporation to dryness in a platinum dish, the resulting Na_2SO_4 weighed 0.5000 g. Calculate the normality of each solution. How many mil-

liliters of the acid would be required to react with 0.5000 g of soda ash containing 50 per cent Na_2CO_3?

Ans. (a) 0.3519 *N* H_2SO_4; (b) 0.3199 *N* NaOH; (c) 13.40 ml.

14. In the standardization of a NaOH solution, 25.00-ml aliquots were titrated with 0.1000 *N* H_2SO_4. The use, on successive portions, of methyl orange, methyl red, and phenolphthalein as indicators required, respectively, 24.90, 24.80, and 24.70 ml of the acid. Calculate (a) the normality of the NaOH solution for each indicator; and (b) the error resulting from the titration of an unknown, using methyl orange as the indicator but with the normality calculated for phenolphthalein.

Ans. (a) 0.09960 *N* (MO); 0.09940 *N* (MR); 0.09880 *N* (Ph); (b) 0.80 per cent.

15. The titration in Problem 14 was repeated with phenolphthalein, but with change of direction. Then 24.80 ml of acid required 25.00 ml of alkali. Calculate the acid/alkali ratio for the two cases. *Ans.* 0.988 and 0.992.

4. *Dilution of Solutions*[20]

For various purposes definite amounts of solution are specified, the solution to have some exact value, such as 10.00 ml of a 0.1000 *N* solution. Unless the solution can be prepared by direct weighing, standardization is necessary by methods discussed in the preceding section. If standardization gives a value such as 0.1015 *N*, either of two alternatives may be followed to get the over-all reactivity of acid represented by the example just given. The 0.1015 *N* solution may be *diluted* to 0.1000 *N* (the subject of this set of problems); or a *conversion factor* may be used, as discussed in the next section.

To make such dilutions, the analyst may start with a given volume of the 0.1015 *N* solution, such as 1000 ml, and calculate the volume of water to add; or he may end the dilution process with a given volume, such as 1000 ml, by diluting a calculated volume of the 0.1015 *N* solution to 1 liter. Reference should be made to Chapter 12 for the merits of the two methods.

The ratios used, involving *present* and *desired* values of solutions, must be expressed in the same terms, such as normality, g/ml, titer, or equivalent volumes. When the two are not on the same basis, a calculation must be made. The most efficient way is to go from the basis of the present solution, such as g/ml, to that of the desired solution, such as titer, or the reverse. In this instance to calculate both to a different basis, such as normality, would be inefficient.

[20] See Chapter 12 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 149.

Example: If 24.00 ml of a solution of $H_2SO_4 \simeq 25.00$ ml of a 0.1050 N solution of NaOH, calculate (a) the milliliters of water required to dilute a liter to make the titer of the acid 0.006000 g in terms of KOH, and (b) the volume of acid to dilute to 1000 ml to make the concentration 0.005000 g H_2SO_4/ml.

(a) The acid has a greater reactivity/ml than the NaOH solution. Therefore, the normality of the acid is $25/24 \times 0.1050$, or 0.1094 N. As the $T_{(KOH)}$ of 1.0000 N acid is 0.05610 g, that for this solution is 0.05610×0.1094, or 0.006137 g. The volume to which 1000 ml of solution of this titer would be diluted to bring the titer down to 0.006000 g is obtained by multiplying the given volume by the ratio, present value (0.006137 g)/desired value (0.006000 g). Then the difference between this volume and the initial volume gives the volume of water to add. Stated in factor-label form (designating present acid as soln. I and desired acid as soln. II)

$$x \text{ ml soln. II} = 1000 \cancel{\text{ml soln. I}} \times \frac{25.00 \cancel{\text{ml NaOH soln.}}}{24.00 \cancel{\text{ml soln. I}}} \times \frac{0.1050 \cancel{\text{meq. NaOH}}}{1 \cancel{\text{ml NaOH soln.}}} \times \frac{0.05610 \cancel{\text{g KOH}}}{1 \cancel{\text{meq. NaOH}}} \times \frac{1 \text{ ml soln. II}}{0.006000 \cancel{\text{g KOH}}}$$

$$= 1022.7 \text{ ml soln. II}$$

$$\text{ml of water to add} = \text{ml soln. II} - \text{ml soln. I}$$

$$= 1022.7 - 1000.0 = 22.7 \text{ ml}$$

(b) Multiplying the present normality 0.1094, calculated above, by the milliequivalent weight of H_2SO_4, 0.04904, gives the present concentration in g/ml, 0.005365. As the end volume, following dilution, is to be 1000 ml, the volume to dilute will be 1000 times the ratio, desired value (0.005000/present value (0.005365). Stated in factor-label form (designating present acid as soln. I and desired acid as soln. II)

$$x \text{ ml soln. I} = 1000 \cancel{\text{ml soln. II}} \times \frac{0.005000 \cancel{\text{g } H_2SO_4}}{1 \cancel{\text{ml soln. II}}} \times \frac{1 \cancel{\text{meq. } H_2SO_4}}{0.04904 \cancel{\text{g } H_2SO_4}} \times \frac{1 \text{ ml soln. I}}{0.1094 \cancel{\text{meq. } H_2SO_4}}$$

$$= 931.9 \text{ ml soln. I}$$

1. If 25.00 ml of HCl solution $\simeq$ 0.3000 g Na_2CO_3, calculate (a) the H_2O/liter to add to make the acid 0.2000 N and (b) the milliliters of acid to dilute to 500 ml to make the CaO titer 0.006000 g.

Ans. (a) 132.0 ml; (b) 472.6 ml.

2. If 30.00 ml of H_2SO_4 solution give a precipitate of 0.3600 g of $BaSO_4$, calculate (a) the H_2O/liter to add to make the acid 0.1000 N, and (b) the

milliliters of acid to dilute to 1000 ml to make the concentration of H_2SO_4 0.004000 g/ml. *Ans.* (a) 28.1 ml; (b) 793.3 ml.

3. A solution of $Ca(OH)_2$ is found to contain 0.004000 g/ml. Calculate (a) the H_2O/liter to add to make the solution 0.1000 N, and (b) the milliliters of solution to dilute to 1000 ml to make each milliliter equivalent to 0.005000 g H_2SO_4. *Ans.* (a) 79.6 ml; (b) 944.5 ml.

4. If 25.00 ml of KOH solution $\simeq$ 30.00 ml of 0.1060 N H_2SO_4, calculate (a) the milliliters of water to add to a liter of hydroxide solution to make its silicon titer 0.0004000 g (see equation 13, page 621), and (b) the milliliters of solution to dilute to 800 ml to make the concentration of KOH 0.004500 g/ml. *Ans.* (a) 487.2 ml; (b) 504.5 ml.

5. If 40.00 ml of Na_2CO_3, containing 0.005000 g/ml, $\simeq$ 35.00 ml of HNO_3 solution, calculate (a) the H_2O/liter to add to make 1 ml of acid equivalent to 0.005000 g KOH, and (b) the milliliters of acid to dilute to 1000 ml to make the solution 0.1000 M. *Ans.* (a) 209.6 ml; (b) 927.6 ml.

5. Conversion Factors[21]

Occasionally the student is directed to use a given volume of a solution of some specified value, such as 10.00 ml of 0.1000 N solution. If, for example, the acid at hand is 0.1015 N, not quite 10.00 ml of the slightly more concentrated solution would be required. The exact volume may be calculated by multiplying or dividing the 10.00 ml by a factor. The multiplying factor in this case would be 1000/1015, and the dividing factor would be 1015/1000. As in the previous section, the terms used for expressing the value of the solution may be normality, g/ml, titer, or equivalent volumes.

Example: A solution of 0.1000 N $Ba(OH)_2$ is needed. Solution I at hand contains 0.008000 g/ml, and solution II has a N_2O_5 titer of 0.006000 g. Calculate (a) the factor by which to *multiply* specified volumes of 0.1000 N solution to obtain equivalent volumes of solution I, and (b) the factor by which to *divide* specified volumes of 0.1000 N solution to obtain equivalent volumes of solution II.

(a) Dividing the concentration, 0.008000 g, by the milliequivalent weight of $Ba(OH)_2$, 0.08569 g, gives 0.09336 for the normality of solution I. As this is less than 0.1000 N, more of this solution would be required than for the 0.1000 N solution. Consequently, the multiplying factor is greater than 1, and it is given by the ratio 10000/9336. Stated in factor-label form

[21] See Chapter 12 for a discussion of this subject.

$$x\,F = \frac{\text{present solution value}}{\text{desired solution value}} = \frac{\dfrac{0.1000 \text{ meq. } Ba(OH)_2}{1 \text{ ml}}}{\dfrac{0.008000 \text{ g } Ba(OH)_2}{1 \text{ ml}} \times \dfrac{1 \text{ meq. } Ba(OH)_2}{0.08569 \text{ g } Ba(OH)_2}}$$

$$= \frac{0.1000 \cancel{\text{meq. } Ba(OH)_2}}{1 \cancel{\text{ml}}} \times \frac{1 \cancel{\text{ml}}}{0.008000 \cancel{\text{g } Ba(OH)_2}} \times \frac{0.08569 \cancel{\text{g } Ba(OH)_2}}{1 \cancel{\text{meq. } Ba(OH)_2}}$$

$$= 1.071$$

(b) As the milliequivalent weight of N_2O_5 ($H_2O + N_2O_5 \rightarrow 2\ HNO_3$) is 108.02/2000, or 0.05401, the titer of 0.1000 N $Ba(OH)_2$ for N_2O_5 is 0.005401 g. A solution having a titer of 0.006000 g is more concentrated, and, consequently, less will be required for a given purpose. Therefore, the dividing factor will be greater than 1. It is given by the ratio 0.006000/0.005401. Stated in factor-label form

$$x\,F = \frac{\text{present solution value}}{\text{desired solution value}} = \frac{\dfrac{0.006000 \text{ g } N_2O_5}{1 \text{ ml}}}{\dfrac{0.1000 \times 0.05401 \text{ g } N_2O_5}{1 \text{ ml}}}$$

$$= \frac{0.006000 \cancel{\text{g } N_2O_5}}{1 \cancel{\text{ml}}} \times \frac{1 \cancel{\text{ml}}}{0.1000 \times 0.05401 \cancel{\text{g } N_2O_5}}$$

$$= 1.111$$

1. For a given determination 0.1200 N H_2SO_4 is specified. Solution I available has a concentration of 0.005500 g/ml, and solution II available has a titer in terms of $Ca(OH)_2$ of 0.004000 g. Calculate (a) the factor by which to *multiply* specified volumes of the 0.1200 N solution to obtain equivalent volumes of solution I, and (b) the factor by which to *divide* specified volumes of the 0.1200 N solution to obtain equivalent volumes of solution II.

Ans. (a) 1.0699; (b) 0.8997.

2. An available solution of KOH contains 0.006000 g/ml. Calculate the factor by which to (a) *multiply* volumes of 0.1000 N alkali to obtain equivalent volumes of the alkali at hand, and (b) *divide* volumes of the alkali at hand to obtain equivalent volumes of a solution having a P_2O_5 titer of 0.004000 g (phenolphthalein is used as the indicator). *Ans.* (a) 0.9350; (b) 1.0537.

3. If 30.00 ml of HCl solution $\simeq$ 28.00 ml of 0.05000 M $Ba(OH)_2$, calculate the factor by which to (a) *multiply* volumes of 0.1000 N acid to obtain equivalent volumes of the acid at hand, and (b) *divide* volumes of an acid the nitrogen titer of which is 0.001500 g to obtain equivalent volumes of the acid at hand. *Ans.* (a) 1.0708; (b) 0.8716.

4. The Reichert-Meissel number of an oil or fat is the number of milliliters of 0.1000 N alkali required to titrate the acids obtained from 5 g of sample. If in a given determination the titrant used were 0.0954 N, by what factor should the buret reading be multiplied to obtain the Reichert-Meissel number?

Ans. 0.954.

6. *Use of Solutions*[22]

Titrimetry is based upon the use of titrants having values expressed in various ways, such as g/ml, normality, molarity, or titer. Titration involves the determination of the amount of such a titrant that reacts with, or is chemically equivalent to, the desired constituent in a sample. Although standardization on either a volume or mass basis may be used, only volume of titrant is considered here.

Calculation of the amount of a desired constituent necessitates knowing the volume of the titrant, its value, and the weight of the sample. For a direct titration these quantities have the following relationship

$$\frac{\text{volume} \times \text{titer} \times 100}{\text{sample weight}} = \text{per cent}$$

The simplicity of a direct-reading setup is presented in the next section. Unless this shortcut is employed, the analyst has the problem of making the calculation indicated by the above relationship.

Although the relationship given is the simplest approach to the calculation, many operators prefer, or have occasion, to use some value of the solution other than titer. Thus, if normality is the specification, the expression becomes

$$\frac{\text{volume} \times \text{normality} \times \text{milliequivalent weight} \times 100}{\text{sample weight}} = \text{per cent}$$

If the specification is grams of titrant solute/ml, the expression is

$$\frac{\text{volume} \times \text{grams/milliliter} \times \text{factor } (F_1) \times 100}{\text{sample weight}} = \text{per cent}$$

The factor (F_1) provides for conversion of g/ml to titer, or to normality. Still another specification might be molarity, in which case the expression is

$$\frac{\text{volume} \times \text{molarity} \times \text{factor } (F_2) \times \text{millimolecular weight} \times 100}{\text{sample weight}} = \text{per cent}$$

The factor (F_2) in this case is the ratio of the numbers of molecules or moles of the desired constituent and of the titrant that are involved in the titration; millimolecular weight (of the desired constituent) is expressed in grams. In the titration of sodium hydroxide with sulfuric acid, for example, the factor is 2 and the millimolecular weight of sodium hydroxide is 0.0400 g.

Examination of all these expressions shows that

[22] See Chapter 12 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, pp. 157, 160, 183.

$$\text{titer} = N \times \text{meq. wt.} = \text{g/ml} \times F_1 = M \times F_2 \times \text{mmol. wt.}$$

Obviously, use of the titer value requires least calculation.

Example 1: If 30.00 ml of a solution containing 0.005000 g H_2SO_4/ml reacts with 0.2000 g of soda ash, calculate the percentage of Na_2CO_3.

A milliliter of the acid is equivalent to 0.005000 × the ratio, mol. wt. Na_2CO_3/mol. wt. H_2SO_4, or 0.005404 g of Na_2CO_3. Using this titer value, we have

$$\frac{\text{volume of } H_2SO_4 \text{ soln.} \times T_{(Na_2CO_3)} \times 100}{\text{grams of sample}} = \text{per cent}$$

or

$$\frac{30.00 \times 0.005404 \times 100}{0.2000} = 81.06 \text{ per cent}$$

Stated in factor-label form

$$x\ \%\ (Na_2CO_3) = (\text{g } Na_2CO_3 \times 100)/\text{g sample}$$

$$= \frac{30.00 \text{ ml. } H_2SO_4}{0.2000 \text{ g sample}} \times \frac{0.005000 \text{ g } H_2SO_4}{1 \text{ ml } H_2SO_4} \times \frac{0.05300 \text{ g } Na_2CO_3}{0.04904 \text{ g } H_2SO_4} \times 100\%$$

$$= 81.06 \text{ per cent}$$

Back titrations complicate such a calculation slightly. An excess of one standard solution is added and the unused portion is then titrated with a second standard solution. If the values of the two solutions are on the same basis in terms of reactivity, such as 0.1000 N, then the difference in volumes is the volume to use in one of the expressions given above. Generally the two values are not on the same basis and some calculation of one of the values must be made before subtraction is possible. Two possibilities of dealing with this complication are illustrated in the example.

Example 2: The nitrogen from 0.5021 g of sample was distilled into 50.00 ml of 0.1880 N H_2SO_4. If the unused acid required 41.30 ml of 0.1765 N NaOH in the back titration, calculate the percentage of nitrogen.

As the two normalities are not the same, the difference in volumes cannot be taken directly. The volume of the NaOH solution times the ratio of the two normalities, 1765/1880, gives the volume of alkali that would have been used if its normality were 0.1880. This volume may then be subtracted from the volume of acid used. The difference is the volume of acid required to react with the ammonia from the nitrogen. From this point on, the calculation is the same as for a direct titration. The overall setup is

$$\% \text{ N} = \frac{[\text{vol. I} - (\text{vol. II} \times N \text{ ratio})] \times N \text{ of acid} \times \text{meq. wt. of N} \times 100}{\text{sample}}$$

$$= \frac{[50.00 - (41.30 \times 0.9338)] \times 0.1880 \times 0.01401 \times 100}{0.5021}$$

$$= 5.89$$

Many prefer to calculate such a problem by the use of milliequivalents. The practice is sound, providing the milliequivalent used is that applying to the reaction involved in the particular titration. In the problem given, the total milliequivalents of acid are 50.00×0.1880, or 9.40 meq. Similarly, the milliequivalents of NaOH are 41.30×0.1765, or 7.29 meq. The difference, $9.40 - 7.29$, is 2.11 meq. This is the amount of acid used. Therefore, this number of milliequivalents of nitrogen must have reacted. Multiplying 2.11 by the milliequivalent weight of nitrogen, 0.01401 g, gives 0.02956 g of nitrogen. Then the percentage is $0.02956/0.5021 \times 100 = 5.89$.

Simple, direct titrations. 1. A sample of 0.4000 g of pearl ash reacted with 50.00 ml of 0.1200 N H_2SO_4. Calculate the percentage of K_2O.

Ans. 70.64 per cent.

2. A sample of vinegar weighing 5.500 g was diluted to 100 ml. If a 25.00-ml aliquot required 15.00 ml of a solution containing 0.002500 g of KOH/ml, what was the percentage of acetic acid ($HC_2H_3O_2$)?

Ans. 2.92 per cent.

3. If a sample of soda ash weighing 1.100 g reacted with 35.00 ml of 0.5000 N H_2SO_4, what is the percentage of CO_2? *Ans.* 35.00 per cent.

4. If a soda ash sample contains 95 per cent Na_2CO_3, what weight of sample should be used so that at least 40 ml of 0.1200 N HCl would be required for the titration? *Ans.* 0.2678 g.

5. A sample of 0.5000 g of soda ash required 48.00 ml of 0.1650 N H_2SO_4. How many wheelbarrows full of soda ash, containing 100 lbs. each, should be put into a 1-ton mix for glass, if the final content of Na_2O in the glass is to be 40 per cent (2.2 lbs. = 1 kg)? *Ans.* 16.3 wheelbarrows full.

6. A sample of 1.115 g of potash lye (KOH) reacted with 40.00 ml of a solution of HCl containing 0.007500 g/ml. What was the percentage of non-alkaline constituents? *Ans.* 58.91 per cent.

7. A sample of 3.200 g of acetic anhydride is diluted to 500 ml. If a 50.00-ml aliquot required 40.50 ml of 0.0510 M $Ba(OH)_2$, what was the purity of the anhydride [$H_2O + (CH_3CO)_2O \rightarrow ?$]. *Ans.* 65.88 per cent.

8. The carbon in 2.000 g of steel was burned to CO_2 and absorbed in excess $Ba(OH)_2$ solution, 75.00 ml of which $\simeq$ 25.00 ml of 0.1500 N HCl solution. If, after absorption of CO_2 from a determination, the same volume of hydroxide required 20.00 ml of the acid, what was the percentage of carbon?

Ans. 0.225 per cent.

9. A sample of mixed carbonates, $SrCO_3$ and Li_2CO_3, weighed 0.5310 g. If it reacted with 20.10 ml of 0.5010 *N* acid, what was the percentage of SrO and of Li_2O? *Ans.* 24.09 per cent SrO; 14.10 per cent Li_2O.

Back titrations. 1. A sample of limestone weighing 0.500 g was dissolved in 50.00 ml of 0.2000 *N* H_2SO_4. If the excess acid required 18.00 ml of 0.1800 *M* NaOH, what was the percentage of CaO? *Ans.* 37.91 per cent.

2. The N_2O_5 evolved from a 0.5000-g sample was absorbed in 50.00 ml of 0.2000 *N* KOH. If the excess alkali required 28.20 ml of HCl solution containing 0.01050 g/ml, calculate the percentage of N_2O_5.

Ans. 20.02 per cent.

3. The nitrogen from 1.400 g of fertilizer was distilled as ammonia into 50.00 ml of H_2SO_4 containing 0.009000 g/ml. The excess acid required 40.00 ml of NaOH, the titer of which was 0.007500 g in terms of H_2SO_4. Calculate the percentage of nitrogen. *Ans.* 3.06 per cent.

4. A meat-scrap sample weighed 2.100 g. The ammonia distilled from it was absorbed in 40.00 ml of 0.6705 *N* HCl. If 34.00 ml of 0.6350 *N* NaOH were required to neutralize the excess acid, what was the percentage of protein (per cent N $\times$ 6.25 = per cent protein)? *Ans.* 21.81 per cent.

5. An analyst is to make 100 Kjeldahl determinations a day for 2 weeks (5.5 days each). What is the minimum number of liters of 0.1 *N* NaOH and H_2SO_4 needed if the ammonia is distilled into 50 ml of the standard acid and the average percentage of nitrogen in the samples of 0.5 g is 1.5?

Ans. 55 liters of H_2SO_4; 50 liters of NaOH.

6. The yellow precipitate containing phosphorus obtained from a 0.5000-g sample of fertilizer was dissolved in 25.00 ml of 0.2015 *M* NaOH. If the excess alkali required 20.00 ml of 0.1820 *N* acid, what was the percentage of P_2O_5 in the sample (see equation 15, page 622)? *Ans.* 8.62 per cent.

Two-indicator titrations.[23] 1. A sample of 4.000 g containing NaOH, Na_2CO_3, and inert matter was diluted to 1 liter. A 50-ml aliquot, titrated at zero degrees with phenolphthalein as the indicator, required 45.00 ml of 0.1000 *N* HCl. On addition of methyl orange and continuation of the titration, 2.00 ml more acid was used. Calculate the percentages of NaOH and Na_2CO_3 (see page 407). *Ans.* 86.00 per cent NaOH; 10.60 per cent Na_2CO_3.

2. A sample of 15.00 g containing mixed NaOH and Na_2CO_3 was diluted to 500 ml. Aliquots of 50 ml were titrated with 0.9500 *N* HCl. The first aliquot required 36.00 ml of acid. The second, following precipitation of CO_3^{-2} ion with excess barium chloride, required 28.00 ml of acid. Calculate the percentages of NaOH and Na_2CO_3.

Ans. 70.93 per cent NaOH; 26.85 per cent Na_2CO_3.

3. Water containing calcium hydrogen carbonate may be softened by adding lime water, the reaction being

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3\downarrow + 2\ H_2O$$

[23] See Exercise 25.5, page 406.

The plant operator aims to come as near stoichiometric treatment as possible, without overtreating. Analytical control measures the effectiveness of the work. Samples presented to the laboratory may contain any of the following: distilled water; $Ca(OH)_2$; $CaCO_3$ (as it is slightly soluble); $Ca(HCO_3)_2 + CaCO_3$; $Ca(OH)_2 + CaCO_3$; and $Ca(HCO_3)_2$. On the basis of Problem 1 of this group, suggest a method to determine what is in the sample and how much of each constituent is present.

4. An analyst has at hand 100 ml each of 8 unmarked solutions, but they are known to be one each of the following: (1) HCl; (2) H_3PO_4; (3) HCl and H_3PO_4; (4) H_3PO_4 and NaH_2PO_4; (5) NaH_2PO_4 and Na_2HPO_4; (6) Na_2HPO_4 and Na_3PO_4; (7) Na_3PO_4; (8) NaOH. Using methyl orange and phenolphthalein indicators, and HCl and NaOH solutions as titrants, suggest a means to identify the solutions and to determine the amount of each constituent. (*Hint:* To one 25-ml portion of each solution add methyl orange, and to another 25-ml portion add phenolphthalein. Titrate each with HCl or NaOH.)

7. *Direct-Reading Solutions*[24]

In order to speed up analytical determinations and to reduce possible errors of calculation, the analyst may set the conditions of titration so that the reading of the buret, in milliliters, is the percentage of the desired constituent. The expression

$$\frac{\text{volume of titrant} \times \text{titer} \times 100}{\text{weight of sample}} = \text{per cent}$$

applies to all simple titrimetric determinations. Obviously, if the sample weight = 100 times the titer value, the buret reading in milliliters is the percentage. Such a titrant is known as a direct-reading solution. A given sample weight fixes the titer, if this relationship holds, and vice versa. The sample weight may be varied easily to fit any given titer, but the reverse is usually not feasible with a given solution.

If the normality of the titrant is involved in the calculation, the general expression becomes

$$\frac{\text{volume} \times \text{normality} \times \text{milliequivalent weight} \times 100}{\text{weight of sample}} = \text{per cent}$$

and $$\text{sample} = \text{normality} \times \text{milliequivalent weight} \times 100$$

The milliequivalent weight is for the *desired constituent* and not for the solute of the titrant.

In order to avoid the inconvenience of using large volumes of titrant necessary for high percentage samples, the analyst may take a simple fraction of a direct-reading sample weight. If the reverse situation prevails

[24] See Chapter 12 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 163.

and too little titrant would be used for reasonable reading errors, a simple multiple of the direct-reading sample weight may be used.

Example 1: A solution of NaOH contains 0.004500 g/ml. Calculate the weight of sample to use to have (a) the volume in milliliters equal directly the percentage of H_3PO_4, and (b) 1 ml = 0.5 per cent HNO_3. Methyl orange is to be used in both cases as the indicator.

(a) With methyl orange as the indicator, all three constituents react mole for mole and we may write

$$\begin{array}{ccc} H_3PO_4 & \simeq & NaOH & \simeq & HNO_3 \\ 63.02 & & 40.00 & & 98.04 \end{array}$$

The g NaOH/ml times the ratio $H_3PO_4/NaOH$ gives the titer of the NaOH in terms of H_3PO_4, or 0.01102 g. Multiplying this value by 100 gives the sample weight in grams. Stated in factor-label form, keeping in mind that in 100 g of sample 1 per cent of H_3PO_4 = 1 g of H_3PO_4

$$x \text{ g sample} = 100 \text{ g sample} \times \frac{1 \text{ ml NaOH soln.}}{1 \text{ g } H_3PO_4} \times \frac{98.04 \text{ g } H_3PO_4}{40.00 \text{ g NaOH}} \times \frac{0.004500 \text{ g NaOH}}{1 \text{ ml NaOH soln.}}$$

$$= 1.102 \text{ g sample}$$

(b) Similarly, the g NaOH/ml times the ratio $HNO_3/NaOH$ gives the titer in terms of HNO_3, or 0.007088 g. Multiplying this value by 100 gives 0.7088 g, the weight of sample to use if volume of titrant = per cent HNO_3 directly. As 1 ml is to equal 0.5 per cent, it is necessary to divide the buret reading by two to obtain the percentage. This step would be necessary only if 2 × 0.7088 g, or 1.418 g, were used for the sample. Stated in factor-label form, keeping in mind that in 100 g of sample 0.5 per cent = 0.5 g

$$x \text{ g sample} = 100 \text{ g sample} \times \frac{1 \text{ ml NaOH soln.}}{0.5000 \text{ g } HNO_3} \times \frac{63.02 \text{ g } HNO_3}{40.00 \text{ g NaOH}} \times \frac{0.004500 \text{ g NaOH}}{1 \text{ ml NaOH soln.}}$$

$$= 1.418 \text{ g sample}$$

If the problem had stated that 1 ml = 2 per cent, then 0.7088/2 would be the required sample weight.

Example 2: Samples of 0.5000 g are specified for the determination of the alkalinity of soda ash. Calculate (a) the normality of a H_2SO_4 titrant if 1 ml = 1 per cent Na_2CO_3, and (b) the Na_2O titer of the acid, if the volume used divided by 2 = per cent Na_2O.

(a) From the equation for the reaction of H_2SO_4 with Na_2CO_3, one may write

$$\begin{array}{ccc} Na_2CO_3 & \simeq & H_2SO_4 \simeq Na_2O \\ 106.00 & & 98.08 \quad 62.00 \end{array}$$

The relationship involving normality ($S = N \times$ meq. wt. $\times$ 100) may be used here. The milliequivalent weight of Na_2CO_3 here is 0.05300 g. Then the desired normality = sample/100 meq. wt., or 0.5000/5.300 = 0.09434.

Another method involves calculating the titer of the titrant. For a 0.5000-g sample, the titer must be 0.005000 g for direct reading. This value divided by the milliequivalent weight, 0.05300 g, gives the normality. Stated in factor-label form

$$x\,N = \frac{\text{meq. } H_2SO_4}{1 \text{ ml soln.}} = \frac{0.005000 \text{ g } Na_2CO_3}{1 \text{ ml soln.}} \times \frac{1 \text{ meq. } H_2SO_4}{0.05300 \text{ g } Na_2CO_3}$$

$$= 0.09434\,N$$

(b) If 1 ml of titrant is to equal 1 per cent of Na_2O for a sample of 0.5000 g, the titer has to be 0.005000 g. In order that division of the volume by two to obtain percentage be necessary, the titer of the solution would have to be one-half that for a direct-reading solution, or 0.005000/2 g. Stated in factor-label form

$$x\,T_{(Na_2O)} = \frac{\text{g } Na_2O}{1 \text{ ml soln.}} = \frac{0.005000 \text{ g } Na_2O}{2 \text{ ml soln.}} = 0.002500 \text{ g/ml soln.}$$

1. If a solution of $Ba(OH)_2$ contains 0.007500 g/ml, what sample weight must be used to have each milliliter = 0.5 per cent N_2O_5? *Ans.* 0.9454 g.

2. If 0.5000-g samples of soda ash are used, what must be the normality of the H_2SO_4 titrant in order for the milliliters of solution, when multiplied by 2, to equal the percentage of Na_2O? *Ans.* 0.3226 *N*.

3. What weight of sample should be used if each milliliter of 0.1500 *N* H_2SO_4 is to equal per cent Na_2CO_3? *Ans.* 0.7950 g.

4. If 0.4000-g samples of K_2CO_3 are used, what must be the concentration of the HCl titrant, in g/ml, in order to have each milliliter equal 2 per cent K_2O? *Ans.* 0.006193 g.

5. If 30.00 ml of NaOH $\simeq$ 27.00 ml of H_2SO_4 containing 0.005000 g/ml, calculate the weight of sample to use if milliliters of alkali equal the percentage of N_2O_5. *Ans.* 0.4955 g.

6. A 0.1050 *N* solution of KOH is used to titrate acids. Calculate the weight of sample to use if (a) the total volume equals the percentage of $KHSO_4$, and (b) each milliliter equals 0.5 per cent $HClO_4$.

Ans. (a) 1.430 g; (b) 2.110 g.

7. A solution of $Ca(OH)_2$ contains 0.002000 g/ml. Calculate the weight of sample to use to have (a) 1 ml = 2 per cent $LiHCO_3$, and (b) the total

volume, when multiplied by 2, equal per cent H_3PO_4 (see equation 7, page 621).

Ans. (a) 0.1834 g; (b) 0.1322 g.

8. A solution of KOH is to be used for titrating acidic solutions. Calculate (a) the normality of the solution if each milliliter equals 0.5 per cent H_2SO_4 when 0.4000-g samples are used; and (b) the sample weight to use if milliliters of 0.1000 *N* solution, divided by 3, equals per cent HNO_3; and (c) the weight of sample to use if each milliliter of 0.1500 *M* alkali equals 2 per cent $H_2C_2O_4$.

Ans. (a) 0.04081 *N*; (b) 1.891 g; (c) 0.3376 g.

9. Free carbon dioxide in water is determined by titrating with NaOH in the presence of phenolphthalein, the reaction being

$$NaOH + H_2O + CO_2 \rightarrow NaHCO_3 + H_2O$$

If 100-ml samples are titrated, what must be the normality of the NaOH to have the total volume, when multiplied by 10, equal the CO_2 in p.p.m.?[25] By what factor should this result be multiplied to obtain the result in p.p.m. of $CaCO_3$? *Ans.* 0.02274 *N*; 2.274.

10. Alkalinity of water may be determined by titration of the calcium and magnesium hydrogen carbonates with a dilute acid. The results often are expressed in terms of calcium carbonate (mol. wt. = 100). If the sample titrated is 100 ml, what must be the normality of the acid to have the volume used, when multiplied by 10, give mg/liter of $CaCO_3$? *Ans.* 0.0200 *N*.

OXIDATION-REDUCTION METHODS[26]

In the discussion of calculations dealing with neutralization methods, the explanation was subdivided in order to emphasize seven kinds of problems. As the same kinds of problems are encountered in all types of titrimetric methods, emphasis henceforth is not directed to this point. Rather, the basis of subdivision for the problems on oxidation-reduction is the reagent used as oxidant or reductant.

In contrast to problems based on neutralization reactions, for oxidation-reduction reactions two points need special attention. In the first place, oxidation-reduction equations often are more involved, with the result that many students do not readily select the significant items upon which a calculation must be based. To aid in understanding the problem, the equation(s) should be written out and the reacting (or equivalent) constituents set apart as being equivalent to each other. In the second place, equivalent weights of oxidants and reductants are usually determined differently and often less readily than those of acids and bases. These two points will be emphasized in the examples given later.

Determination of the fraction of the molecular weight of an oxidant or

[25] Parts per million (p.p.m.) is very close to milligrams per liter in dilute solutions.

[26] See Chapters 12, 14, and 26 for general discussions of this subject; also see Hamilton and Simpson, *op. cit.*, p. 192.

reductant to use as the equivalent weight may be made in several ways. Two of these are suggested as being effective (the section on equivalent weights in Chapter 14 should be reviewed at this point). Briefly, the student has a choice of reasoning in terms of equations for the half-cell reactions involved, or of the oxidation number of the constituents undergoing change, as represented in full equations.

As a general example, the oxidation of iron (II) with dichromate ion may be cited. The molecular equation is

$$K_2Cr_2O_7 + 6\ FeCl_2 + 14\ HCl \rightarrow 2\ CrCl_3 + 6\ FeCl_3 + 2\ KCl + 7\ H_2O$$

The half-cell equation for the oxidant is

$$Cr_2O_7^{-2} + 14\ H^+ + 6\ e \rightleftharpoons 2\ Cr^{+3} + 7\ H_2O$$

and that for the reductant is

$$Fe^{+3} + 1\ e \rightleftharpoons Fe^{+2}$$

As the number of electrons involved per ion is the number by which to divide the molecular weight to obtain an equivalent weight, it is evident that $K_2Cr_2O_7/6$ is the equivalent weight for the dichromate. The equivalent weight of the iron, of course, is the atomic weight.

Alternatively, examination of the molecular equation shows that the chromium in the oxidizing ion $Cr_2O_7^{-2}$ and the iron of the reducing ion Fe^{+2} undergo a change in oxidation number. The number representing the total change is the same as the number of electrons involved in the half-cell equations. Thus, in $K_2Cr_2O_7$ the oxidation state of each Cr atom is +6, if that of each K is +1 and that of O is −2. Then the total oxidation numbers of the two Cr atoms is 12. As these atoms change to the tervalent state in the reaction, there is a change of 3 per atom, or a total change of 6. Note that the actual valence of the *ion* is not involved.

$KMnO_4$ as an Oxidant[27]

Reference to Table 14.1 (page 223) shows that the permanganate ion has four different equivalent weights, the fraction of the molecular weight depending upon whether 1, 3, 4, or 5 electrons react. Of these possibilities, that involving 5 electrons, the typical behavior in acidic solutions, is by far the most important in terms of possible applications. The determination of iron by this method is the best-known example.

Example: If 25.00 ml of $KMnO_4$ solution react with 0.4000 g of $Na_2C_2O_4$, calculate (a) the $KMnO_4$ concentration in g/ml, (b) the normality of the solution, (c) the iron titer, and (d) the weight of sample to use to have 1 ml = 1 per cent CaO.

[27] See Hamilton and Simpson, *op. cit.*, p. 198.

As the reactivity of $KMnO_4$ is required in terms of $Na_2C_2O_4$, Fe, and CaO, equations 1 and 6 (page 645) should be inspected. From them it is evident that one may write

$$2\ KMnO_4 \eqsim 5\ Na_2C_2O_4 \eqsim 10\ Fe \eqsim 5\ CaO$$

and $$2(158.03) \eqsim 5(134.01) \eqsim 10(55.85) \eqsim 5(56.08)$$

Dividing by 10, $$31.61 \eqsim 67.00 \eqsim 55.85 \eqsim 28.04$$

The division by 10 is necessary, to obtain the respective equivalent weights, as 10 electrons are transferred in the reduction of two molecules of permanganate, and, therefore, also in the oxidation of the number of molecules of another substance that reacts directly or indirectly with two molecules of permanganate.

(a) Dividing the mass of oxalate by the equivalent volume of $KMnO_4$ gives the titer in terms of sodium oxalate. Multiplying this value by the ratio of permanganate to oxalate gives the g $KMnO_4$/ml. Stated in factor-label form

$$x\ \text{g } KMnO_4\text{/ml soln.} = \frac{0.4000\ \cancel{\text{g } Na_2C_2O_4}}{25.00\ \text{ml soln.}} \times \frac{31.61\ \text{g } KMnO_4}{67.00\ \cancel{\text{g } Na_2C_2O_4}}$$

$$= 0.007549\ \text{g } KMnO_4\text{/ml soln.}$$

(b) The normality is obtained by dividing the present concentration, 0.007549 g/ml, by that for a normal solution, 0.03161 g/ml. Stated in factor-label form

$$x\ N = \frac{\text{meq. } KMnO_4}{1\ \text{ml soln.}} = \frac{0.007549\ \cancel{\text{g } KMnO_4}}{1\ \text{ml soln.}} \times \frac{1\ \text{meq. } KMnO_4}{0.03161\ \cancel{\text{g } KMnO_4}}$$

$$= 0.2383\ N$$

(c) The titer in terms of iron is most easily obtained by using the normality just calculated. It is the product of this normality, 0.2383, and the milliequivalent weight of Fe, 0.05585 g, or 0.01331 g.

The titer might be calculated from the original data; using the factor-label form

$$x\ \text{g Fe/ml} = \frac{0.4000\ \text{g } Na_2C_2O_4}{25.00\ \text{ml}} \times \frac{55.85\ \text{g Fe}}{67.00\ \cancel{\text{g } Na_2C_2O_4}}$$

$$= 0.01331\ \text{g Fe/ml}$$

(d) As the sample weight for a direct reading solution must equal 100 $T_{(CaO)}$, the CaO titer is needed. As in (c) titer equals $N \times$ meq. wt., or 0.2383×0.02804 g, which gives 0.006820 g. Therefore, the required sample weight is 0.6820 g.

Equivalent weights. Calculate the equivalent weight of the constituent indicated in boldface type in each of the following equations:

1. $2\ \mathbf{KMnO_4} + 10\ FeSO_4 + 8\ H_2SO_4 \rightarrow$
$5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O$
2. $2\ \mathbf{KMnO_4} + 3\ MnSO_4 + 2\ H_2O \rightarrow 5\ MnO_2 + K_2SO_4 + 2\ H_2SO_4$
3. $2\ \mathbf{KMnO_4} + 5\ \mathbf{H_2O_2} + 3\ H_2SO_4 \rightarrow$
$5\ O_2\uparrow + 2\ MnSO_4 + 8\ H_2O + K_2SO_4$
4. $2\ \mathbf{KMnO_4} + 5\ \mathbf{U}(SO_4)_2 + 2\ H_2O \rightarrow$
$5\ UO_2SO_4 + 2\ KHSO_4 + 2\ MnSO_4 + H_2SO_4$
5. $2\ \mathbf{KMnO_4} + 5\ H_3\mathbf{As}O_3 + 3\ H_2SO_4 \rightarrow$
$5\ H_3AsO_4 + 2\ MnSO_4 + K_2SO_4 + 3\ H_2O$
6. $\mathbf{Ca}C_2O_4 + H_2SO_4 \rightarrow CaSO_4 + H_2C_2O_4$
$2\ \mathbf{KMnO_4} + 5\ \mathbf{H_2C_2O_4} + 3\ H_2SO_4 \rightarrow$
$K_2SO_4 + 2\ MnSO_4 + 10\ CO_2\uparrow + 8\ H_2O$
7. $2\ \mathbf{KMnO_4} + 5\ \mathbf{V_2O_2}(SO_4)_2 + 22\ H_2O \rightarrow$
$10\ H_3VO_4 + 2\ MnSO_4 + K_2SO_4 + 7\ H_2SO_4$
8. $4\ \mathbf{KMnO_4} + 5\ \mathbf{Sb_2}(SO_4)_3 + 24\ H_2O \rightarrow$
$10\ H_3SbO_4 + 2\ K_2SO_4 + 9\ H_2SO_4 + 4\ MnSO_4$

1. A solution contains 5.000 g of $KMnO_4$/liter. Calculate its titer in terms of (a) Mn (see equation 2), (b) Fe_2O_3 (see equation 1), and (c) V_2O_5 (see equation 7). *Ans.* (a) 0.002602 g; (b) 0.01263 g; (c) 0.01439 g.

2. If 30.00 ml of $KMnO_4 \approx 0.36.00$ g of As_2O_3 (see equation 5), calculate the oxidant's titer in terms of (a) Fe (see equation 1). (b) H_2O_2 (see equation 3), and (c) Sb (see equation 8).

Ans. (a) 0.01355 g; (b) 0.004127 g; (c) 0.01477 g.

3. If 25.00 ml of $KMnO_4 \approx 0.6000$ g of $Na_2C_2O_4$ (see equation 6), calculate (a) the normality of the $KMnO_4$, (b) the U_3O_8 titer (see equation 4), and (c) the weight of sample to use to have 1 ml = 0.5 per cent Fe.

Ans. (a) 0.3582 *N*; (b) 0.05028 g; (c) 4.000 g.

4. If 40.00 ml of $KMnO_4 \approx 0.4800$ g of $CaCO_3$ (Ca precipitated as the oxalate, and the $C_2O_4^{-2}$ ions titrated—see equation 6), calculate (a) the normality of the titrant, (b) the H_2O/liter needed to bring the concentration down to 0.005000 g/ml, and (c) the weight of sample to use to have each milliliter equal 1 per cent Sb_2O_4 (see equation 8).

Ans. (a) 0.2398 *N*; (b) 516.1 ml; (c) 1.843 g.

5. Calculate the weight of $Fe(SO_4)\cdot(NH_4)_2SO_4\cdot 6H_2O$ that will just react with 35.00 ml of $KMnO_4$, each milliliter of which $\approx$ 0.005000 g of Fe (see equation 1). *Ans.* 1.229 g.

6. If the oxalate ions derived from the calcium precipitated from a 0.5000-g Ca sample require 25.00 ml of 0.1200 *N* $KMnO_4$, what is the percentage of calcium? *Ans.* 12.02 per cent.

7. An iron ore sample of 0.4000 g required 40.00 ml of a solution of $KMnO_4$ containing 0.003000 g/ml. Calculate the percentage of iron.

Ans. 53.01 per cent.

8. If 10.00 ml of H_2O_2 solution (sp. gr. = 1) reacted with 22.00 ml of

$KMnO_4$, for which the $T_{(Fe)}$ was 0.005000 g, calculate the percentage of H_2O_2, and the volume of oxygen that would be liberated (standard conditions).

Ans. 0.33 per cent; 22.06 ml.

9. A powder was known to contain $H_2C_2O_4 \cdot 2H_2O$, inert matter, and $KHC_2O_4 \cdot H_2O$. One sample of 0.5000 g required 39.35 ml of 0.1000 *N* KOH, and another of the same weight required 33.65 ml of 0.2000 *N* $KMnO_4$. Calculate the percentage of each active constituent.

Ans. 14.3 per cent acid; 81.7 per cent hydrogen oxalate.

10. A sample of 0.5000 g of MnO_2 was treated with 100.0 ml of a solution containing 0.005000 g of $H_2C_2O_4 \cdot 2\ H_2O$/ml. If the excess required 20.00 ml of 0.0950 *N* $KMnO_4$, calculate the percentage of Mn (see equation 6).

$$MnO_2 + H_2C_2O_4 + 2\ H^+ \rightarrow Mn^{+2} + 2\ CO_2 \uparrow + 2\ H_2O$$

Ans. 33.15 per cent.

11. A sample of 0.4000 g of PbO_2 was treated with 50.00 ml of H_2O_2 solution, 25.00 ml. of which $\simeq$ 20.00 ml of 0.1000 *N* $KMnO_4$. If 8.00 ml of $KMnO_4$ were required to titrate the excess H_2O_2, calculate the percentage of Pb (see equation 3).

$$PbO_2 + H_2O_2 + 2\ H^+ \rightarrow Pb^{+2} + 2\ H_2O + O_2 \uparrow$$

Ans. 82.88 per cent.

$K_2Cr_2O_7$ as an Oxidant[28]

As an oxidant in acidic solution the chromium in dichromate ion changes oxidation number from +6 to +3, the tervalent chromium ion being the end product under ordinary conditions. As explained already, the equivalent weight is then $K_2Cr_2O_7/6$ g, since two chromium atoms react per ion.

Example: If 6.000 g of $K_2Cr_2O_7$ are diluted to 1000 ml, what is (a) the normality, (b) the iron titer, and (c) the weight of iron ore to use to have 1 ml = 1 per cent Fe_2O_3?

(a) The actual g/liter divided by the weight for a liter of a normal solution gives the normality. Stated in factor-label form

$$x\ N = \frac{\text{g } K_2Cr_2O_7}{1\text{ g eq. } K_2Cr_2O_7} = \frac{6.000\text{ g } K_2Cr_2O_7}{1\ \cancel{\text{liter}}} \times \frac{1\ \cancel{\text{liter}}}{49.04\text{ g eq. } K_2Cr_2O_7}$$

$$= 0.1223\ N$$

(b) This normality, 0.1223, times the milliequivalent weight of Fe, 0.05585, gives the Fe titer, 0.006830 g.

Another method is to multiply the g/ml, 0.006000, by the ratio eq. wt. Fe/eq. wt. $K_2Cr_2O_7$, or 55.85/49.04.

[28] Hamilton and Simpson, *op. cit.*, p. 203.

(c) If 1 ml is to equal 1 per cent Fe_2O_3, the sample must weigh $100 \times T_{(Fe_2O_3)}$. The required titer, as in (b) is the normality × meq. wt. Stated in factor form, where for a 100-g sample, 1 per cent Fe_2O_3 = 1 g Fe_2O_3 = 1 ml of $K_2Cr_2O_7$ soln.,

$$x \text{ g sample} = 100 \text{ g sample} \times \frac{1\ \%\ Fe_2O_3}{1\ g\ Fe_2O_3} \times \frac{1\ ml\ K_2Cr_2O_7\ soln.}{1\ \%\ Fe_2O_3} \times \frac{0.006000\ g\ K_2Cr_2O_7}{1\ ml\ K_2Cr_2O_7\ soln.} \times \frac{1\ eq.\ Fe}{49.04\ g\ K_2Cr_2O_7} \times \frac{79.85\ g\ Fe_2O_3}{1\ eq.\ Fe}$$

$$= 0.9766 \text{ g sample}$$

Equivalent weights. Calculate the equivalent weight of the constituent indicated in boldface type in each of the following equations:

1. $\mathbf{K_2Cr_2O_7} + 6\ \mathbf{FeCl_2} + 14\ HCl \rightarrow 2\ CrCl_3 + 6\ FeCl_3 + 2\ KCl + 7\ \mathbf{H_2O}$
2. $\mathbf{K_2Cr_2O_7} + 3\ \mathbf{H_2SnCl_4} + 14\ HCl \rightarrow 2\ CrCl_3 + 3\ H_2SnCl_6 + 2\ KCl + 7\ \mathbf{H_2O}$
3. $\mathbf{K_2Cr_2O_7} + 9\ KI + 14\ HCl \rightarrow 2\ CrCl_3 + 3\ KI(I_2) + 8\ KCl + 7\ H_2O$
4. $\mathbf{K_2Cr_2O_7} + 3\ \mathbf{UCl_4} + 2\ HCl \rightarrow 2\ CrCl_3 + 3\ UO_2Cl_2 + 2\ KCl + H_2O$

1. Calculate the weight of $K_2Cr_2O_7$ (purity factor = 1.004) for 500 ml of a solution the iron titer of which is to be 0.005000 g. *Ans.* 2.186 g.

2. N.B.S. Sample No. 26 contains 58.62 per cent iron. If 0.2500 g requires 25.61 ml of a solution containing 0.005000 g $K_2Cr_2O_7$/ml, what is the purity factor of the dichromate? *Ans.* 100.5 per cent.

3. A solution of $K_2Cr_2O_7$ contains 5.000 g/liter. Calculate (a) the normality, the $T_{(FeO)}$, and (c) the weight of hematite ore sample to be used for the volume of titrant, when multiplied by 2, to equal percentage of Fe_2O_3.

Ans. (a) 0.1020 *N*; (b) 0.007329 g; (c) 0.4072 g.

4. If a sample of 0.5000 g is to be used, how many grams of pure $K_2Cr_2O_7$ should be dissolved in making 500 ml of a solution in order to have each milliliter equal 2 per cent Fe_3O_4? *Ans.* 3.177 g.

5. If each milliliter of $K_2Cr_2O_7$ is to equal 1 per cent U_3O_8, when a 0.5000-g sample is used, what must be the concentration of the titrant in g/ml?

Ans. 0.001746 g.

6. If 41.20 ml of 0.1200 *N* $K_2Cr_2O_7$ react with the iron in a 0.5000-g sample of ore, what was the percentage of iron? *Ans.* 55.22 per cent.

7. If 40.00 ml of a solution containing 0.01600 g $FeSO_4$/ml were added to reduce the chromate obtained on fusing 0.2500 g of Cr ore, and if the excess reductant required 30.00 ml of 0.1200 *N* $K_2Cr_2O_7$, calculate the percentage of chromium (for equations, see Exercise 26.7, page 432). *Ans.* 4.25 per cent.

KI_3 as an Oxidant[29]

As it is necessary to have a considerable concentration of iodide ions present in order to dissolve iodine in water, the active ion formed is

[29] Hamilton and Simpson, *op. cit.*, p. 212.

assumed to be triiodide I_3^-. In order to interpret the calculations that apply to the system, the author uses the formula $KI(I_2)$. This is to keep clear that only two of the iodine atoms change oxidation state, as shown in the half-cell equation

$$(I_2)\ I^- + 2\ e \rightleftharpoons 3\ I^-$$

Evidently two iodine atoms take on one electron each to become iodide ions. Therefore, the equivalent weight of the iodine reacting is its atomic weight, 126.92 g.

Example: An "iodine" solution is prepared by dissolving 7.000 g of resublimed iodine in a solution of potassium iodide, and diluting it to 500 ml. Calculate (a) the normality, (b) the $T_{(As)}$, and (c) the volume equivalent to 25.00 ml of 0.0950 N $Na_2S_2O_3$ solution.

(a) The concentration in g/ml is 7.000/500, or 0.01400 g. The concentration in g/ml of a 1.000 N solution is 126.92/1000, or 0.1269 g. The actual concentration/the concentration for a normal solution gives the normality, or 0.01400/0.1269 = 0.1103 N.

(b) Reference to equation 3 below shows that the two iodine atoms reacting ≡ As. Therefore, the equivalent weight of As is 74.91/2, or 37.45 g. The $T_{(As)}$ is obtained by multiplying the g I/ml by the ratio, equivalent weight of As/equivalent weight of iodine, which gives in factor-label form

$$x \text{ g As/ml} = \frac{0.01400 \cancel{\text{g I}}}{1 \text{ ml}} \times \frac{74.91 \text{ g As}}{2 \cancel{\text{eq. wt.}}} \times \frac{1 \cancel{\text{eq. wt.}}}{126.92 \cancel{\text{g I}}}$$

$$= 0.004131 \text{ g As/ml}$$

(c) The volume equivalent to 25.00 ml of 0.0950 N $Na_2S_2O_3$ is found by multiplying the stated volume by the ratio of the two normalities, which in factor-label form is

$$x \text{ ml} = 25.00 \text{ ml} \times \frac{0.0950\ N}{0.1103\ N} = 21.53 \text{ ml}$$

Equivalent weights. Calculate the equivalent weight of the constituent indicated in boldface type in each of the following equations:

1. $KI(\mathbf{I_2}) + 2\ Na_2S_2O_3 \rightarrow 2\ NaI + KI + Na_2S_4O_6$
2. $KI(\mathbf{I_2}) + \mathbf{H_2S} \rightarrow 2\ HI + KI + S$
3. $KI(I_2) + \mathbf{H_3AsO_3} + H_2O \rightarrow H_3AsO_4 + 2\ HI + KI$
4. $2\ \mathbf{Cu}(C_2H_3O_2)_2 + 5\ KI \rightarrow 2\ CuI\downarrow + KI(I_2) + 4\ KC_2H_3O_2$
5. $KI(I_2) + H_2\mathbf{Sn}Cl_4 + 2\ HCl \rightarrow H_2SnCl_6 + KI + 2\ HI$
6. $KI(I_2) + H_3\mathbf{Sb}O_3 + H_2O \rightarrow H_3SbO_4 + 2\ HI + KI$
7. $KI(I_2) + \mathbf{Na_2CS_3} \rightarrow CS_2 + S + 2\ NaI + KI$
8. $KI(I_2) + \mathbf{SO_2} + 2\ H_2O \rightarrow 2\ HI + KI + H_2SO_4$

1. The H_2S evolved from a sample of 5.000 g of steel required 1.90 ml of an "iodine" solution, the titer of which, in terms of As_2O_3, was 0.004945 g. Calculate the percentage of S in the steel (see equations 2 and 3).

Ans. 0.061 per cent.

2. A standard steel contains 0.05 per cent of S. The H_2S evolved by treatment with HCl is titrated with an "iodine" solution, 45.00 ml of which react with 24.00 ml of 0.0900 *N* $Na_2S_2O_3$. How many milliliters will be required in using this "iodine" solution for a 5.00-g sample of steel. *Ans.* 3.23 ml.

3. If 30.00 ml of "iodine" solution are equivalent to 0.1500 g of As_2O_3, calculate (a) the H_2O/liter to add to make the solution 0.1000 *N*, and (b) the volume needed to dilute to a liter to make the $T_{(Sn)} = 0.005000$ g (see equations 3 and 5). *Ans.* (a) 11.1 ml; (b) 833.2 ml.

4. What weight of sample of an antimony alloy should be taken if the volume of a 0.0935 *N* "iodine" solution, when multiplied by 2, is to equal the percentage of antimony? *Ans.* 0.2846 g.

5. An "iodine" solution of unknown concentration is used to titrate the H_2S in water (see equation 2); 25.00 ml of the $KI(I_2)$ $\approx$ 22.50 ml of a $Na_2S_2O_3$ solution (see equation 1); and 25.00 ml of the $Na_2S_2O_3$ solution react with the iodine liberated by 23.00 ml of 0.1000 *N* $K_2Cr_2O_7$, according to the equation

$$K_2Cr_2O_7 + 9\ KI + 14\ HCl \rightarrow 2\ CrCl_3 + 3\ KI(I_2) + 8\ KCl + 7\ H_2O$$

Calculate the titer of the "iodine" solution in terms of H_2S. *Ans.* 0.001411 g.

6. A sample of 1.000 g of mixed sodium sulfide and sodium thiocarbonate, following oxidation with Na_2O_2, gave a precipitate of 1.750 g of $BaSO_4$. Another sample of the same mass, following dissolution in water, reacted with 60.00 ml of 0.0940 *N* "iodine" solution (see equations 2 and 7). Calculate the percentages of Na_2CS_3 and Na_2S.

Ans. 3.76 per cent Na_2S; 36.06 per cent Na_2CS_3.

Cerate as an Oxidant[30]

Although the Ce (III) $\rightleftharpoons$ Ce (IV) transformation has usually been expressed by the simple half-cell equation

$$Ce^{+3} \rightleftharpoons Ce^{+4} + 1\ e$$

there is evidence[31] that the reaction is more complicated, the oxidant being actually a complex anion (see Chapter 26). In a sulfuric acid solution, for example, this anion is probably $Ce(SO_4)_3^{-2}$. In the following problems only sulfuric acid solutions of cerium are considered, but other acid solutions can be used in which there presumably exist complex anions, such as $Ce(NO_3)_6^{-2}$.

As one electron per ion is involved in the half-cell equation, the equiva-

[30] Hamilton and Simpson, *op. cit.*, p. 205.

[31] See Diehl and Smith, *Quantitative Analysis*, pp. 270-281, Wiley, 1952.

lent weight of cerium is the atomic weight, 140.13 g. Reasoning in terms of oxidation state yields the same result.

Example: If 30.00 ml of cerate solution ≃ 0.3600 g of $Na_2C_2O_4$ (see equation 2, below), calculate (a) the g/ml of cerium, (b) the normality, and (c) the iron titer.

(a) The weight of $Na_2C_2O_4$ divided by the volume of titrant gives directly the $Na_2C_2O_4$ titer. Multiplying this value by the ratio of cerium to oxalate gives the concentration of Ce/ml. In factor-label form this is

$$x \text{ g Ce/ml} = \frac{0.3600 \cancel{\text{ g } Na_2C_2O_4}}{30.00 \text{ ml}} \times \frac{2(140.13) \text{ g Ce}}{134.01 \cancel{\text{ g } Na_2C_2O_4}}$$

$$= 0.01763 \text{ g Ce/ml}$$

(b) The actual concentration, 0.01763 g/ml, divided by the concentration for a 0.1000 *N* solution, 0.1401 g, gives the normality, 0.1258 *N*.

(c) This normality times the milliequivalent weight of Fe gives the $T_{(Fe)}$, or $0.1258 \times 0.05585 = 0.007026$ g (see equation 1, below).

Equivalent weights. Calculate the equivalent weights of each constituent indicated in boldface type in the following equations:

1. $2\ \mathbf{H_2Ce(SO_4)_3} + 2\ FeSO_4 \rightarrow Ce_2(SO_4)_3 + Fe_2(SO_4)_3 + 2\ H_2SO_4$
2. $2\ \mathbf{H_2Ce(SO_4)_3} + Na_2C_2O_4 \rightarrow 2\ CO_2\uparrow + Ce_2(SO_4)_3 + Na_2SO_4 + 2\ H_2SO_4$
3. $2\ H_2Ce(SO_4)_3 + \mathbf{H_3AsO_3} + H_2O \rightarrow H_3AsO_4 + Ce_2(SO_4)_3 + 3\ H_2SO_4$
4. $2\ H_2Ce(SO_4)_3 + \mathbf{H_2O_2} \rightarrow Ce_2(SO_4)_3 + 3\ H_2SO_4 + O_2\uparrow$

1. A solution contains 45.00 g of $(NH_4)_2Ce(NO_3)_6$ per liter. Calculate (a) the titer in terms of As (see equation 3), and (b) the weight of sample to use to have 1 ml = 1 per cent FeO. *Ans.* (a) 0.003074 g; (b) 0.5897 g.

2. Calculate the weight of $Na_2C_2O_4$ required to react with 35.00 ml of a solution of $H_2Ce(SO_4)_3$, each milliliter of which is to be equivalent to 0.005000 g of Fe (see equations 1 and 2). *Ans.* 0.2099 g.

3. If 30.00 ml of the solution for Problem 1 reacted with the iron in a 0.5000-g sample of ore, what was the percentage of Fe_2O_3? *Ans.* 39.32 per cent.

Other Oxidants

Various other oxidants have had more or less use. The equations given here show typical applications of them. The calculations involved are of the same general nature as those for the oxidants considered thus far. The specific problem in any case is to determine the equivalent weight, if desired, or the reacting ratio of oxidant to desired constituent.

Equivalent weights. Calculate the equivalent weight[32] of the constituent indicated in boldface type in each of the following equations:

[32] In order to determine the equivalent weight of the iodate or bromate shown in the equations, make a careful check of the changes in oxidation state of the reactants. Table 14.1 (page 223) shows the number of electrons involved in the half-cell reactions.

1. $\mathbf{KIO_3} + 2\ H_2\mathbf{SnCl_4} + 6\ HCl \rightarrow 2\ H_2SnCl_6 + KCl + ICl + 3\ H_2O$
2. $\mathbf{KIO_3} + 2\ \mathbf{SO_2} + 2\ HCl + H_2O \rightarrow 2\ H_2SO_4 + KCl + ICl$
3. $\mathbf{KIO_3} + 8\ KI + 6\ HCl \rightarrow 3\ KI(I_2) + 6\ KCl + 3\ H_2O$
4. $7\ \mathbf{KIO_3} + 4\ Cu\mathbf{SCN} + 14\ HCl \rightarrow 4\ HCN + 4\ CuSO_4 + 7\ ICl + 7\ KCl + 5\ H_2O$
5. $\mathbf{KH(IO_3)_2} + 16\ KI + 11\ HCl \rightarrow 11\ KCl + 6\ H_2O + 6\ KI(I_2)$
6. $\mathbf{KBrO_3} + 3\ Na_3\mathbf{AsO_3} + (HCl) \rightarrow KBr + 3\ Na_3AsO_4$
7. $\mathbf{KBrO_3} + 5\ KBr + 6\ HCl \rightarrow 6\ KCl + 3\ H_2O + 3\ Br_2\uparrow$
8. $\mathbf{KBrO_3} + 3\ \mathbf{SbCl_3} + 6\ HCl \rightarrow 3\ SbCl_5 + KBr + 3\ H_2O$

$Na_2S_2O_3$ as a Reductant[33]

Sodium thiosulfate is probably unique in titrimetry in that, although it is one of the most widely used titrants, it has only one direct reaction. This one application has already been discussed in Chapters 14 and 26, but it is so important that the equation is repeated:

$$2\ Na_2S_2O_3 + KI(I_2) \rightarrow Na_2S_4O_6 + 2\ NaI + KI$$

The wide use of sodium thiosulfate in titrimetry rests on the fact that many oxidants liberate an equivalent amount of iodine from excess iodide ions. Titration of the liberated iodine, according to the above equation, is the basis for the calculation of the amount of the oxidizing agent. Subsequent equations represent examples of some of the applications.

It was noted in the discussion of iodimetry that 1 gram-atom of iodine and 1 gram-molecule of sodium thiosulfate each represent an equivalent weight. Comparison of the oxidizing agent with the thiosulfate in any given equation will serve to indicate the equivalent weight of the oxidant.

Example: If 25.00 ml of $Na_2S_2O_3$ solution react with 0.4000 g of iodine dissolved in excess KI, calculate (a) the concentration in g/ml, (b) the normality, (c) the copper titer, and (d) the weight of sample to use to have 1 ml = 1 per cent of Mn (see equations below).

(a) The weight of iodine, 0.4000 g, divided by the volume of titrant gives directly the iodine titer. This value times the ratio of $Na_2S_2O_3/I$ gives the concentration of $Na_2S_2O_3$ in g/ml. Stated in factor-label form

$$x\ \text{g}\ Na_2S_2O_3/\text{ml} = \frac{0.4000\ \cancel{\text{g I}}}{25.00\ \text{ml}} \times \frac{158.13\ \text{g}\ Na_2S_2O_3}{126.92\ \cancel{\text{g I}}}$$

$$= 0.01206\ \text{g}\ Na_2S_2O_3/\text{ml}$$

(b) The present concentration, 0.01206 g/ml, divided by the concentration for a normal solution, 0.15813 g/ml, gives the normality, or 0.07627 *N*.

[33] See Hamilton and Simpson, *op. cit.*, p. 203. This section also contains problems on iodine as an oxidant.

(c) The copper titer equals the normality, 0.07627, times the milliequivalent weight of Cu, 0.06354 g, or 0.004846 g.

(d) If 1 ml = 1 per cent Mn, the value of 100 $T_{(Mn)}$ is needed for the sample weight. To obtain the Mn titer, first note the following relationship of Mn to $Na_2S_2O_3$ (see equations 8 and 9 below):

$$MnO_2 \simeq Mn \simeq 2\ Cl \simeq 2\ I \simeq 2\ S_2O_3^{-2}$$

As $Mn/2 \simeq Na_2S_2O_3 \simeq I$, we may go directly from the $T_{(I)}$ to $T_{(Mn)}$. Stated in factor-label form

$$x\ g\ Mn/ml = \frac{0.4000\ \cancel{g\ I}}{25.00\ ml} \times \frac{54.93/2\ g\ Mn}{126.92\ \cancel{g\ I}} = 0.03462\ g\ Mn/ml$$

Therefore, 100 × 0.03462 g, or 3.462 g, is the sample weight of pyrolusite, MnO_2, to use.

Equivalent weights. Calculate the equivalent weight of the constituent indicated in boldface type in each of the following equations, keeping in mind that the iodine liberated is titrated with thiosulfate according to equation 8:

1. $\mathbf{K_2Cr_2O_7} + 9\ KI + 14\ HCl \rightarrow 3\ KI(I_2) + 2\ CrCl_3 + 8\ KCl + 7\ H_2O$
2. $2\ \mathbf{KMnO_4} + 15\ KI + 8\ H_2SO_4 \rightarrow 5\ KI(I_2) + 2\ MnSO_4 + 6\ K_2SO_4 + 8\ H_2O$
3. $\mathbf{H_2O_2} + 3\ KI + H_2SO_4 \rightarrow KI(I_2) + K_2SO_4 + 2\ H_2O$
4. $2\ \mathbf{Cu}(C_2H_3O_2)_2 + 5\ KI \rightarrow KI(I_2) + 2\ CuI\downarrow + 4\ KC_2H_3O_2$
5. $\mathbf{KBrO_3} + 9\ KI + 6\ HCl \rightarrow 3\ KI(I_2) + KBr + 6\ KCl + 3\ H_2O$
6. $\mathbf{Cl_2} + 3\ KI \rightarrow KI(I_2) + 2\ KCl$
7. $\mathbf{KIO_3} + 8\ KI + 6\ HCl \rightarrow 3\ KI(I_2) + 6\ KCl + 3\ H_2O$
8. $2\ \mathbf{Na_2S_2O_3} + KI(I_2) \rightarrow Na_2S_4O_6 + 2\ NaI + KI$
9. $\mathbf{MnO_2} + 4\ HCl \rightarrow MnCl_2 + 2\ H_2O + Cl_2\uparrow$
   $Cl_2 + 3\ KI \rightarrow KI(I_2) + 2\ KCl$
10. $\mathbf{H_3AsO_4} + 2\ HI + KI \rightarrow KI(I_2) + H_3AsO_3 + H_2O$
11. $2\ \mathbf{CeO_2} + 8\ HCl + 3\ KI \rightarrow KI(I_2) + 2\ KCl + 2\ CeCl_3 + 4\ H_2O$
12. $2\ \mathbf{H_3VO_4} + 2\ HBr + 4\ HCl \rightarrow Br_2\uparrow + (VO)_2Cl_4 + 6\ H_2O$
    $Br_2 + 3\ KI \rightarrow KI(I_2) + 2\ KBr$
13. $\mathbf{KIO_4} + 11\ KI + 8\ HCl \rightarrow 4\ KI(I_2) + 8\ KCl + 4\ H_2O$
14. $O_3 + 3\ KI + H_2O \rightarrow KI(I_2) + 2\ KOH + O_2\uparrow$
15. $2\ \mathbf{K_3Fe(CN)_6} + 3\ KI \rightarrow KI(I_2) + 2\ K_4Fe(CN)_6$
16. $2\ \mathbf{FeCl_3} + 3\ KI \rightarrow KI(I_2) + 2\ KCl + 2\ FeCl_2$

1. A solution contains 25.00 g $Na_2S_2O_3 \cdot 5\ H_2O$ per liter. Calculate (a) the normality, (b) the copper titer, and (c) the weight of sample to use to have 1 ml = 1 per cent MnO_2 (see equations 8 and 9).

Ans. (a) 0.1007 N; (b) 0.006400 g; (c) 0.4379 g.

2. If 32.00 ml of $Na_2S_2O_3$ solution $\simeq$ 25.00 ml of a solution containing 25.00 g of $CuSO_4 \cdot 5\ H_2O$/liter, calculate (a) the normality of the thiosulfate solution,

(b) its $T_{(I)}$, and (c) the weight of sample to use to have 1 ml = 1 per cent V_2O_5 (see equation 12). *Ans.* (a) 0.07822 *N*; (b) 0.009928 g; (c) 0.7114 g.

3. If 50.00 ml of a solution of $Na_2S_2O_3$ react with the iodine liberated from excess KI solution by 0.4000 g of KIO_3, what is (a) the normality of the titrant, and (b) its titer in terms of As_2O_3 (see equations 7 and 10)?

Ans. (a) 0.2243 *N*; (b) 0.01109 g.

4. Thirty-five milliliters of a solution of $Na_2S_2O_3$ react with the iodine liberated by the action on a KI solution of 30.00 ml of a solution of $K_2Cr_2O_7$, each milliliter of which is equivalent to 0.005000 g Fe. For the thiosulfate solution calculate (a) the normality, (b) the H_2O_2 titer, and (c) the weight of sample to use to have 1 ml = 0.5 per cent Fe (see equations 1, 3, and 16).

Ans. (a) 0.07674 g *N*; (b) 0.001305 g; (c) 0.8572 g.

5. An ore contained 22 per cent Cu. If a sample of 0.6000 g required 25.00 ml of thiosulfate solution, what was the titrant's normality (see equation 4)?

Ans. 0.08310 *N*.

6. The Cu in a 0.2500-g sample liberates enough iodine to require 16.50 ml of $Na_2S_2O_3$ solution. What is the percentage of copper, if 1 ml of the thiosulfate $\doteq$ 0.003620 g $KBrO_3$ (see equations 4 and 5)? *Ans.* 54.55 per cent.

7. If 0.3000-g samples were used in the determination of Cu, and if the volume of thiosulfate, when multiplied by 2, equalled the percentage of Cu, what was the titrant's normality? *Ans.* 0.09443 *N*.

8. A sample of MnO_2 of 0.4000 g required 70.00 ml of 0.0985 *N* thiosulfate solution to titrate the iodine liberated on boiling the ore with HCl solution and passing the evolved chlorine into KI solution. Calculate the percentage of MnO_2 (see equation 9). *Ans.* 74.93 per cent.

9. Calculate the normality of the acid, and its CaO titer, if 30.00 ml of H_2SO_4 $\doteq$ 25.00 ml of 0.1200 *N* $Na_2S_2O_3$. In addition to equation 8, the following reaction is involved:

$$KIO_3 + 8\ KI + 3\ H_2SO_4 \rightarrow 3\ KI(I_2) + 3\ K_2SO_4 + 3\ H_2O$$

Ans. 0.1000 *N*; 0.002804 g.

10. If 50,000 ml of a suspension formed by diluting 5.000 g of bleaching powder to 1000 ml required 35.00 ml of 0.1000 *N* sodium thiosulfate to titrate the liberated iodine, calculate the percentage of chlorine available according to the equations

$$CaCl\cdot ClO + 2\ HC_2H_3O_2 \rightarrow Ca(C_2H_3O_2)_2 + H_2O + Cl_2\uparrow$$
$$Cl_2 + 3\ KI \rightarrow KI(I_2) + 2\ KCl$$

Ans. 49.64 per cent.

11. How much formic acid is equivalent to 80.00 ml of 0.1200 *N* thiosulfate according to the equations

$$HCOOH \rightarrow H_2O + CO\uparrow$$
$$5\ CO + I_2O_5 \rightarrow I_2 + 5\ CO_2\uparrow$$

Ans. 1.104 g.

Other Reductants

As stated in Chapters 14 and 26, various factors make oxidants more generally used than reductants as standard solutions. However, there is available a considerable variety of possible reductants. Some of them, such as sodium arsenite and titanium (III) chloride, are used for the direct titration of oxidants. Others, such as iron (II) sulfate, oxalic acid, and hydrogen peroxide, are usually added in excess and the unused excess is back-titrated with an oxidant.

In general, the reactions involved are those represented by equations already given under particular oxidants. However, in order to emphasize some of these reductants, we repeat a few equations here, in reverse order. No problems are included, as they would be quite similar to those for the oxidants.

Equivalent weights. Calculate the equivalent weight for the constituent indicated in boldface type in each of the following equations:

1. $6\ \mathbf{FeSO_4} + K_2Cr_2O_7 + 7\ H_2SO_4 \rightarrow 3\ Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7\ H_2O$
2. $\mathbf{H_2SnCl_4} + 2\ FeCl_3 \rightarrow H_2SnCl_6 + 2\ FeCl_2$
3. $\mathbf{Na_3AsO_3} + HClO \rightarrow Na_3AsO_4 + HCl$
4. $\mathbf{TiCl_3} + FeCl_3 \rightarrow TiCl_4 + FeCl_2$
5. $2\ TiCl_3 + \mathbf{H_2O_2} + 2\ HCl \rightarrow 2\ TiCl_4 + 2\ H_2O$
6. $\mathbf{CrCl_2} + FeCl_3 \rightarrow CrCl_3 + FeCl_2$
7. $\mathbf{UCl_4} + 2\ FeCl_3 + 2\ H_2O \rightarrow UO_2Cl_2 + 2\ FeCl_2 + 4\ HCl$
8. $\mathbf{H_2C_2O_4} + MnO_2 + H_2SO_4 \rightarrow MnSO_4 + 2\ H_2O + 2\ CO_2\uparrow$
9. $\mathbf{H_2O_2} + PbO_2 + 2\ HNO_3 \rightarrow Pb(NO_3)_2 + 2\ H_2O + O_2\uparrow$

PRECIPITATION AND COMPLEXATION METHODS[34]

Many reactions go to practical analytical completion as a result of the formation of an insoluble precipitate, or of a soluble complex of high stability. The use of silver nitrate for titrating chloride ions illustrates the precipitation type; the use of potassium cyanide for titrating nickel illustrates the second type. That so few of the seemingly feasible reactions in this group are in actual use is probably attributable to the lack of ready means for detecting end points.

As emphasized in Chapter 15, there seems no simple, sure way for deciding what is an equivalent weight for some of the reactants. Potassium cyanide, for example, is a very confusing case.

Example: One gram of pure nickel was dissolved and diluted to 250 ml. If a 25.00-ml aliquot reacted with 30.00 ml of KCN solution, according to

[34] See Chapters 12, 15, and 27 for a general discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 222 for precipitimetry and p. 227 for complexiметry.

equation 5 below, calculate for the cyanide solution its (a) concentration in g/ml, (b) molarity, (c) normality, and (d) Ag titer.

(a) As a 1/10 aliquot was used, 0.1000 g of nickel reacted with the KCN, and 1 ml of titrant is equivalent to 0.003333 g Ni. Multiplying this value by the factor 4 KCN/Ni gives the g KCN/ml. Stated in factor-label form

$$x \text{ g KCN/ml KCN soln.} = \frac{1.0000 \cancel{\text{ g Ni}}}{250 \cancel{\text{ ml Ni soln.}}} \times \frac{25.00 \cancel{\text{ ml Ni soln.}}}{30.00 \text{ ml KCN soln.}} \times \frac{4 \cancel{\text{ mole KCN}}}{1 \cancel{\text{ mole Ni}}} \times \frac{1 \cancel{\text{ mole Ni}}}{58.69 \cancel{\text{ g Ni}}} \times \frac{65.11 \text{ g KCN}}{1 \cancel{\text{ mole KCN}}}$$

$$= 0.01479 \text{ g KCN/ml KCN soln.}$$

(b) The g/ml calculated in (a) divided by the gram-millimolar weight of KCN, 0.06511 g, gives the molarity, 0.2272 *M*.

(c) Calculation of the normality serves as an example of the dilemma encountered with KCN solutions. Reference may be made to the various equations below for examples of variation in the way this reagent functions in terms of the valence of several metals. If the K^+ and the CN^- ions are considered as univalent, and therefore equivalent to 1.008 g of hydrogen, the normality is the same as the molarity in (b). But if the bivalent nickel involved in the reaction is considered, then 2 KCN are concerned for each valence of the nickel. Then the normality would be one-half of the molarity. As stated earlier, the safe way is to avoid normality and deal in terms of molarity or titer.

(d) It is assumed that the silver ion is to be titrated with the KCN. Consequently, equation 3 below applies. Then the g KCN/ml in (a) multiplied by the factor Ag/KCN gives the silver titer.

Molar and equivalent weights. Calculate the molar weight, and the equivalent weight where possible, for the constituent indicated in boldface type in each of the following equations:

1. $KBr + \mathbf{AgNO_3} \rightarrow KNO_3 + AgBr\downarrow$
2. $2\ \mathbf{KCN} + \mathbf{AgNO_3} \rightarrow KAg(CN)_2 + KNO_3$
3. $\mathbf{KCN} + \mathbf{AgNO_3} \rightarrow KNO_3 + AgCN\downarrow$
4. $\mathbf{Co}(NO_3)_2 + 2\ \mathbf{KCN} \rightarrow 2\ KNO_3 + Co(CN)_2\downarrow$
5. $\mathbf{Ni}(NH_3)_4Cl_2 + 4\ KCN \rightarrow K_2Ni(CN)_4 + 2\ KCl + 6\ NH_3\uparrow$
6. $2\ \mathbf{Cu}(NH_3)_4Cl_2 + 7\ \mathbf{KCN} + H_2O \rightarrow K_4[Cu_2(CN)_6] + KCNO + 2\ KCl + 2\ NH_4Cl + 6\ NH_3\uparrow$
7. $\mathbf{NaCl} + \mathbf{AgNO_3} \rightarrow NaNO_3 + AgCl\downarrow$
8. $\mathbf{KSCN} + \mathbf{AgNO_3} \rightarrow KNO_3 + AgSCN\downarrow$
9. $K_3\mathbf{AsO_4} + 3\ \mathbf{AgNO_3} \rightarrow 3\ KNO_3 + Ag_3AsO_4\downarrow$

10. $Ag_3\mathbf{As}O_4 + 3\ HNO_3 \rightarrow 3\ AgNO_3 + H_3AsO_4$
$AgNO_3 + \mathbf{KSCN} \rightarrow KNO_3 + AgSCN\downarrow$
11. $KH_2PO_4 + \mathbf{UO_2}(C_2H_3O_2)_2 \rightarrow HC_2H_3O_2 + KC_2H_3O_2 + UO_2HPO_4\downarrow$
12. $\mathbf{Pb}(NO_3)_2 + \mathbf{(NH_4)_2MoO_4} \rightarrow 2\ NH_4NO_3 + PbMoO_4\downarrow$
13. $3\ \mathbf{Zn}Cl_2 + 2\ \mathbf{K_4Fe(CN)_6} \rightarrow K_2Zn_3[Fe(CN)_6]_2 + 6\ KCl$
14. $2\ \mathbf{Ba}Cl_2 + \mathbf{K_2Cr_2O_7} + H_2O \rightarrow 2\ KCl + 2\ HCl + 2\ BaCrO_4\downarrow$
15. $\mathbf{Ca}Cl_2 + 2\ \mathbf{C_{15}H_{31}COOK} \rightarrow 2\ KCl + Ca(C_{15}H_{31}COO)_2\downarrow$

1. Calculate the weight of $AgNO_3$ required for 750 ml of a solution each milliliter of which = 0.001000 g Cl. *Ans.* 3.593 g.

2. If 30.00 ml of $AgNO_3$ solution react with 0.1800 g of NaCl, calculate (a) the H_2O/liter necessary to make the solution 0.1000 *N*, and (b) the weight of sample necessary for 1 ml = 2 per cent Cl. *Ans.* (a) 26.5 ml; (b) 0.1820 g.

3. If 30.00 ml of a solution of $(NH_4)_2MoO_4$ give a precipitate of 0.9000 g of $PbMoO_4$, calculate (a) the molarity of the solution, and (b) its titer in terms of Pb_3O_4. *Ans.* (a) 0.08170 *M*; (b) 0.01867 g.

4. If 25.00 ml of a solution of KCN give a precipitate of 0.5000 g of AgCN, calculate the titers in terms of Ag, Co, Ni, and Cu (see equations 3, 4, 5, and 6). *Ans.* 0.01612 g Ag; 0.004402 g Co; 0.002192 g Ni; 0.002712 g Cu.

5. The concentration of $K_4Fe(CN)_6$ is 0.04000 g/ml. Calculate (a) the molarity, and (b) the weight of sample to use in order that 1 ml = 0.5 per cent ZnO. *Ans.* (a) 0.1086 *M*; (b) 2.652 g.

6. To a 0.4000-g sample of chloride were added 40.00 ml of 0.1250 *M* $AgNO_3$. The back-titration of the excess $AgNO_3$ solution required 10.00 ml of 0.1050 *N* KSCN (Volhard method). Calculate the percentage of Cl. *Ans.* 35.09 per cent.

7. If the NaCl titer of a solution of $AgNO_3$ is to be 10 mg., how many grams of salt must be dissolved to make 500 ml of solution, and what will be its normality? *Ans.* 14.54 g; 0.1711 *N*.

8. If 25.00 ml of 0.1200 *M* KH_2PO_4 reacts with the uranium in a sample of 0.8500 g, calculate the percentage of U_3O_8. *Ans.* 99.09 per cent.

9. A sample of tombstone weighing 1.500 g yielded a mixture of 0.1015 g of KCl and NaCl. If 30.00 ml of 0.05080 *N* $AgNO_3$ reacted with the Cl, calculate the percentages of Na and K. *Ans.* 2.00 per cent K; 1.16 per cent Na.

10. In the titration of Cl^- ion in water analysis 50.00-ml samples are used. What must be the Cl titer of the $AgNO_3$ solution, if the milliliters used, when multiplied by 0.5 give milligrams of Cl? *Ans.* 0.500 mg.

GRAVIMETRIC CONVERSION FACTORS[35]

A gravimetric factor is the number by which to multiply a given mass of a substance to obtain the chemically equivalent mass of another substance. Thus, 40.08 g of calcium will form 56.08 g of calcium oxide, the reaction being

[35] See Hamilton and Simpson, *op. cit.*, p. 93.

$$2\ Ca + O_2 \rightarrow 2\ CaO$$

The factor for converting unit mass of Ca to CaO is CaO/Ca, or 1.3992, and the factor for making the reverse calculation is Ca/CaO, or 0.71469.

In the example, $Ca \longleftrightarrow CaO$, the ratio is 1:1. When such a ratio is not 1:1, care must be taken to use the correct coefficients. The general rule in such cases is to balance the numerator and denominator of the fraction in terms of the constituent *concerned.* Thus, if iron is weighed as Fe_2O_3, the factor for Fe in Fe_2O_3 is $2\ Fe/Fe_2O_3$, as iron is obviously the desired constituent. If the factor for converting unit mass of Fe_2O_3 to Fe_3O_4 is wanted, both iron and oxygen are common elements in numerator and denominator. The element *concerned,* however, is iron and not oxygen. Therefore, the factor must be $2\ Fe_3O_4/3\ Fe_2O_3$, in order for the number of iron atoms to balance. Incidentally, in such multiplying factors the denominator of the fraction is the constituent *from* which one is going and the numerator is the constituent *to* which one is going.

If the factor involves formulas containing no common constituents or if the relationship is otherwise not immediately obvious, the factor can be calculated by setting up a chain showing the stoichiometric relation of the principal items in the reactions involved. For example, the arsenic in a given sample is oxidized to arsenate which is precipitated as the silver salt. The latter compound is dissolved in acid and the silver is precipitated as silver chloride which is weighed. The problem is to calculate the As_2O_3 equivalent to the arsenic in the sample from the weight of AgCl found. The weight of As_2O_3 will equal the weight of the AgCl multiplied by the factor for converting AgCl to As_2O_3. The transformations concerned are

$$As_2O_3 \rightarrow 2\ As \rightarrow 2\ Ag_3AsO_4 \rightarrow 6\ Ag \rightarrow 6\ AgCl$$

The factor, therefore, is $As_2O_3/6AgCl$.

Gravimetric factors are of sufficient practical importance that extensive tables have been compiled for ready use for a large number of transformations.[36] Usually the logarithm of the factor is included to facilitate the calculations when logarithms are employed.

1. Calculate the factors for the transformations indicated.

(a) MgO in $Mg_2P_2O_7$
(b) NH_3 in $(NH_4)_2SO_4$
(c) KCl in K_2PtCl_6
(d) Li_2O in Li_3PO_4
(e) MnO_2 in Mn_3O_4
(f) $Na_2B_4O_7$ from KBF_4
(g) Pb_3O_4 from $PbSO_4$
(h) K_2O from KCl
(i) P_2O_5 from $Mg_2P_2O_7$
(j) Fe_3O_4 from Fe_2O_3
(k) $Mg_2As_2O_7$ to K_3AsO_4
(l) $BaSO_4$ to H_2SO_4
(m) $KClO_4$ to K_2O
(n) $Mg_2P_2O_7$ to $MgCO_3$
(o) Pt to K_2O [37]

[36] See Caley, *Analytical Factors and Their Logarithms,* Wiley, 1932; Hodgman, *Handbook of Chemistry and Physics,* Chemical Rubber Co., 1954; Lange, *Handbook of Chemistry,* Handbook, 1952.

[37] $K_2O \rightarrow 2\ KCl \rightarrow K_2PtCl_6 \rightarrow Pt$.

Ans. (a) 0.3621 (f) 0.3996 (k) 1.651
(b) 0.2577 (g) 0.7536 (l) 0.4202
(c) 0.3067 (h) 0.6317 (m) 0.3399
(d) 0.3869 (i) 0.6379 (n) 0.7573
(e) 1.140 (j) 0.9666 (o) 0.4825

2. Copy the accompanying table in the laboratory notebook at the beginning of the section devoted to gravimetric measurements. Calculate to five significant figures the values needed for the blank columns. The first line is filled in as an example.

SOME FACTORS AND THEIR LOGARITHMS

Log Factor	*Factor*	*Transformation*	*Factor*	*Log Factor*
9.83555-10	0.68163	$HCl \leftrightarrow NH_4Cl$	1.4671	10.16645-10
		$Ag \leftrightarrow AgCl$		
		$Al \leftrightarrow Al_2O_3$		
		$Ba \leftrightarrow BaSO_4$		
		$Cl \leftrightarrow AgCl$		
		$Ca \leftrightarrow CaCO_3$		
		$Ca \leftrightarrow CaO$		
		$Fe \leftrightarrow Fe_2O_3$		
		$FeO \leftrightarrow Fe_2O_3$		
		$Mg \leftrightarrow Mg_2P_2O_7$		
		$MgCO_3 \leftrightarrow Mg_2P_2O_7$		
		$MgO \leftrightarrow Mg_2P_2O_7$		
		$P \leftrightarrow Mg_2P_2O_7$		
		$P_2O_5 \leftrightarrow Mg_2P_2O_7$		
		$Ni \leftrightarrow Ni(C_4H_7O_2N_2)_2$		
		$S \leftrightarrow BaSO_4$		
		$SO_4 \leftrightarrow BaSO_4$		
		$Zn \leftrightarrow ZnNH_4PO_4$		

3. If lead is weighed as $PbSO_4$, calculate the gravimetric factors for lead in the forms: (a) ordinary lead (207.21), (b) lead from uranium (206), and (c) lead from thorium (208). *Ans.* (a) 0.6832; (b) 0.6820; (c) 0.6845.

4. Uranium is often weighed as U_3O_8. Calculate the gravimetric factor for (a) ordinary uranium (238.07), and (b) for fissionable uranium (235).

Ans. (a) 0.8480; (b) 0.8463.

USE OF SIMPLE FACTORS IN CALCULATING PERCENTAGES

In precipitation-gravimetric methods the product weighed may be the desired constituent itself, as gold or selenium. Generally, the product is some compound of the constituent which, if pure, bears a definite known relationship to the desired constituent. Thus, chlorine is weighed as silver chloride.

The general relationship for the calculation of percentages in all such cases is

$$\frac{\text{weight of residue} \times \text{factor} \times 100}{\text{weight of sample}} = \text{per cent}$$

The factor is the number by which to multiply the mass of the substance weighed (the residue) to obtain the chemically equivalent mass of the desired substance. In the few cases where the desired substance is the substance weighed, the factor is unity, of course.

Example: If 1.200 g of coal yields 0.1050 g of $BaSO_4$ what is the percentage of sulfur?

The factor for sulfur in $BaSO_4$ is $S/BaSO_4$ or 0.1374. Substituting the known values in the general expression gives

$$\frac{0.1050 \text{ g} \times 0.1374 \times 100}{1.200 \text{ g}} = 1.20 \text{ per cent}$$

1. A sample of 0.5000 g yielded 1.1570 g of a precipitate of AgCl. Calculate the percentage of chlorine. *Ans.* 57.25 per cent.

2. If 2.000 g of material gave a precipitate of 0.5000 g of ammonium molybdophosphate, $(NH_4)_3(P[Mo_3O_{10}]_4)$, what was the percentage of P_2O_5? *Ans.* 1.89 per cent.

3. A sample of uranium-bearing material weighing 0.8000 g yielded 0.2000 g of U_3O_8. Calculate the percentage of uranium. *Ans.* 21.21 per cent.

4. Analysis of a sample of 0.5000 g of brass gave, in succession, the following amounts of substances: 0.0330 g of SnO_2; 0.0277 g of PbO_2; 0.3465 g of Cu; 0.2756 g of $ZnNH_4PO_4$; and 0.0123 g of $Ni(C_4H_7O_2N_2)_2$. Calculate the percentages of the five metals.

Ans. Sn, 5.20; Pb, 4.80; Cu, 69.30; Zn, 20.20; Ni, 0.50 per cent.

5. Analysis of a sample of 0.8000 g of limestone yielded the following weights of products: loss on ignition (CO_2), 0.3216 g; 0.0100 g of SiO_2; 0.0020 g of MnO_2; 0.6983 g of $CaCO_3$; 0.1877 g of $Mg_2P_2O_7$; and 0.0206 g of K_2PtCl_6. Calculate the percentages of CO_2, SiO_2, Mn_3O_4, CaO, MgO, and K_2O.

Ans. CO_2, 40.20; SiO_2, 1.25; Mn_3O_4, 0.66; CaO, 48.90; MgO, 8.50; K_2O, 0.50 per cent.

DIRECT-READING OR FACTOR WEIGHT SAMPLES[38]

In the discussion of titrimetric calculations it was stated that the relationship

$$\frac{\text{volume of titrant} \times \text{titer} \times 100}{\text{weight of sample}} = \text{per cent}$$

is the most efficient to use. When the sample weight $= 100\ T$, the volume in milliliters equals the percentage directly.

[38] See Hamilton and Simpson, *op. cit.*, p. 98.

In direct precipitation-gravimetric calculations a similar relationship applies:

$$\frac{\text{weight of residue} \times \text{factor} \times 100}{\text{weight of sample}} = \text{per cent}$$

Here a direct-reading sample is taken as one numerically equal to the factor. Thus, if calcium is weighed as the oxide, the factor for calcium is Ca/CaO, or 0.7147. In contrast to titrimetric calculations, the 100 is handled differently. To include it with the factor, as is done in the 100 T for direct-reading titrimetric samples, would give a sample too large to handle. Actually, if the residue and the sample weight are expressed in the same units, the decimal point need only be moved two places to the right in order for the weight of residue to equal percentage. A weight of 0.4255 g of CaO, for example, becomes 42.55 per cent Ca.

As in titrimetric determinations, such a factor weight of sample may be too large for high-analysis materials or too small for low-analysis materials. If this situation arises, one uses, respectively, a simple fraction or simple multiple of the direct-reading value. This point is illustrated in the following example.

Example: The magnesium in limestone may be precipitated as $MgNH_4PO_4 \cdot 6\ H_2O$ and weighed as $Mg_2P_2O_7$, following ignition at 900°. Calculate the grams of sample to use to have (a) the residue in grams ($\times$ 100) equal per cent Mg, (b) the residue in grams when divided by 2 (and $\times$ 100) equal per cent MgO, (c) the residue in grams when multiplied by 3 (and $\times$ 100) equal per cent $MgCO_3$, and (d) each milligram of residue equal 0.1 per cent Mg.

(a) First, the factor for Mg, 2 $Mg/Mg_2P_2O_7$, or 0.2185, is needed. As the residue multiplied by 100 is to equal the percentage, the sample must equal the factor, 0.2185 g.

(b) Here the factor needed is 2 $MgO/Mg_2P_2O_7$, or 0.3623. If the residue multiplied by 100 were to read the percentage directly, the sample weight would be 0.3623 g. As the product must be divided by 2, the sample would have to be 2 $\times$ 0.3623, or 0.7246 g.

(c) The factor in this case is 2 $MgCO_3/Mg_2P_2O_7$, or 0.7577. If the residue multiplied by 100 were to read percentage directly, the sample would be 0.7577 g. As the product must be multiplied by 3, the sample would have to be 0.7577/3, or 0.2526 g.

(d) Here the same factor is used as in (a), or 0.2185. As the weight of residue is expressed in milligrams, the 100 has already been taken into account (if the sample weight remains expressed in grams). Therefore, the sample weight equals the factor, 0.2185 g.

1. If phosphorus is weighed as $Mg_2P_2O_7$, what weight of sample should be used for the residue to (a) equal the percentage when divided by 2 (and $\times$ 100), and (b) equal the percentage of P_2O_5 when multiplied by 2 (and $\times$ 100)?

Ans. (a) 0.5567 g; (b) 0.3189 g.

2. Arsenic may be weighed as $Mg_2As_2O_7$. What weight of sample would be used to have (a) the residue in grams (and $\times$ 100) equal the percentage of As, and (b) each milligram of residue equal 0.2 per cent As_2O_3?

Ans. (a) 0.4826 g; (b) 0.3186 g.

3. The iron in magnetite is weighed as Fe_2O_3. What weight of sample should be taken to have (a) the residue in grams (and $\times$ 100) equal the percentage of Fe_3O_4, and (b) the residue in grams when multiplied by 2 (and $\times$ 100) equal the percentage of Fe? *Ans.* (a) 0.9666 g; (b) 0.3497 g.

4. What weights of sphalerite must be used to have each milligram of residue equal 0.1 per cent Zn when the Zn is weighed as (a) ZnO, (b) $ZnNH_4PO_4$, and (c) $Zn_2P_2O_7$? *Ans.* (a) 0.8034 g; (b) 0.3665 g; (c) 0.4291 g.

5. What weights of lead ore should be weighed to have the weight of residue of $PbSO_4$, in grams ($\times$ 100) equal the percentage of (a) Pb, (b) PbO when multiplied by 2, and (c) Pb_3O_4 when divided by 3?

Ans. (a) 0.6832 g; (b) 0.3679 g; (c) 2.261 g.

6. The sulfur in a sample is oxidized to sulfate and weighed as $BaSO_4$. What weight of sample should be taken to have the residue in grams ($\times$ 100) equal the percentage of (a) S when divided by 3, (b) SO_3 when multiplied by 2, and (c) SO_4? *Ans.* (a) 0.4122 g; (b) 0.1715 g; (c) 0.4115 g.

7. The calcium in limestone is weighed as CaO. Calculate the weight of sample to use to have (a) the residue in grams, when multiplied by 2 (and $\times$ 100), equal per cent Ca, (b) the residue in grams, when divided by 2 (and $\times$ 100), equal per cent $CaCO_3$, and (c) each milligram of residue equal 0.1 per cent CaO.

Ans. (a) 0.3572 g; (b) 3.569 g; (c) 1.0000 g.

8. What weights of spiegel must be taken for analysis to have each milligram of $Mn_2P_2O_7$ equal (a) 0.2, (b) 0.1, and (c) 0.05 per cent Mn?

Ans. (a) 0.1935 g; (b) 0.3871 g; (c) 0.7742 g.

9. If an impure sample of NaCl yielded a precipitate of AgCl weighing the same amount as the sample, what was the percentage purity of the material?

Ans. 40.78 per cent.

CONCURRENT POLYCOMPONENT DETERMINATIONS[39]

In some analytical situations it is difficult to, or advantageous not to, separate each constituent and to measure it. Occasionally, suitable methods of separation or of specific measurement are lacking. In such eventualities, it is often possible to analyze a sample for n constituents by making n measurements where each of the determined values comprises the behavior of from 1 to n of the components. These n numerical values

[39] See Chapter 28, Exercise 28.8, for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 108.

then enable one to set up and to solve n simultaneous equations containing n unknowns, that is, to calculate the amounts of n constituents.

Often, one of the equations is provided by the fact that the sum of the desired constituents equals the whole sample. Other equations are derived in various ways, depending upon the specific properties of the elements or compounds concerned. Some of these ways include (1) converting the sample to another form, e.g., a mixture of metal chlorides to the sulfates and reweighing; (2) determining a constituent common to two components, e.g., weighing the AgCl derived from a mixture of NaCl and KCl; (3) carrying out a specific determination on one constituent of a mixture, e.g., titrating the Fe in a mixture of Fe_2O_3 and Al_2O_3. The measurements are often indirect determinations.

In such indirect determinations the desired constituent, or a compound of it, is not measured directly. Instead, the measurement is made on some constituent that is known to be chemically equivalent to the desired constituent. A good example is the permanganimetric determination of calcium. The calcium is first precipitated as the oxalate. Then, following dissolution in sulfuric acid, the oxalate ion is titrated with permanganate. The calculation is based on the assumption that there was a calcium ion for each oxalate ion titrated. As another example, all measurements with thiosulfate, except that of triiodide ion itself, are of this general type.

Example 1: A combined residue of 0.2500 g of Al_2O_3 and Fe_2O_3 was obtained from 1.0500 g of molding sand. When the iron in the mixture was dissolved and reduced, it reacted with 11.00 ml of 0.1000 N $KMnO_4$. Calculate the percentage of iron and of aluminum.

This problem illustrates the determination of the noncommon element in a known mixture. As 1 ml of 0.1000 N $KMnO_4 \simeq 0.007985$ g of Fe_2O_3, 11.00 ml would react with 0.0878 g. Then the sum of the two oxides, 0.2500 g, minus 0.0878 g equals 0.1622 g, the weight of the Al_2O_3. The percentage of each constituent is then calculated in the usual way.

Example 2: A sample of 1.5000 g of a substance containing bromine and chlorine yielded 1.0000 g of a precipitate of AgBr and AgCl. On chlorination of this mixed halide precipitate, the loss in weight was 0.1300 g. Calculate the percentages of Br and Cl.

The solution of this problem will be illustrated algebraically. Also it will be used as an example of the calculation of the indirect factors to be found in handbooks of chemical data.

Let $x =$ weight of Cl and $y =$ weight of Br; also let $a =$ weight of mixed AgCl and AgBr found on precipitation with $AgNO_3$, and $b =$

weight of total AgCl remaining after the Br in the AgBr was replaced by Cl.

Then, $x\left(\frac{\text{AgCl}}{\text{Cl}}\right)$ = weight of AgCl in the mixture

$y\left(\frac{\text{AgBr}}{\text{Br}}\right)$ = weight of AgBr in the mixture

$$x\left(\frac{\text{AgCl}}{\text{Cl}}\right) + y\left(\frac{\text{AgBr}}{\text{Br}}\right) = a \text{ (1.0000 g in the problem given)} \quad (33.1)$$

On chlorination, the AgBr is converted to AgCl, or

$y\left(\frac{\text{AgBr}}{\text{Br}}\right) \times \left(\frac{\text{AgCl}}{\text{AgBr}}\right)$ = AgCl formed from the AgBr

$x\left(\frac{\text{AgCl}}{\text{Cl}}\right)$ = AgCl formed originally

$$x\left(\frac{\text{AgCl}}{\text{Cl}}\right) + y\left(\frac{\text{AgCl}}{\text{Br}}\right) = b \text{ (0.8700 g in the problem given)} \quad (33.2)$$

By substitution of the appropriate numerical values for the known atomic and molecular weights, such as Cl and AgBr, equations (33.1) and (33.2) become

$$4.043\,x - 2.350\,y = a \quad (33.3)$$
$$4.043\,x - 1.794\,y = b \quad (33.4)$$

and $x = 1.048\,b - 0.8006\,a$ and $y = 1.789\,(a - b)$. These expressions of x and y in terms of a and b are known as "indirect factors."

With the use of these factors and the known weights of a, b, and the sample, the remaining calculation of the percentages is simple. The percentage of Cl is 7.41 and that of Br is 15.58.

1. In accordance with Example 2, calculate the indirect factors for the other two binary mixed halide combinations, that is, chloride + iodide, and bromide + iodide. Let x = weight of the element of smaller atomic weight, y = weight of the element of larger atomic weight, a = weight of mixed silver halides, and b = weight of AgCl after chlorination.

Ans. Cl + I: $x = 0.6350\,b - 0.3876\,a$,
$y = 1.3875\,(a - b)$.
Br + I: $x = 2.7849\,b - 1.7001\,a$,
$y = 2.7001\,a - 3.5375\,b$.

2. A mixture of 0.2500 g of NaCl and KCl was obtained from a sample of 1.5000 g of rock. From this mixture 0.1750 g of $KClO_4$ was obtained. Calculate the percentages of Na_2O and K_2O in the rock.

Ans. 3.97 per cent K_2O; 5.50 per cent Na_2O.

3. A sample of 2.000 g of limestone gave a mixture of 0.2000 g of NaCl

and KCl. This mixture in turn yielded 0.4000 g of AgCl on precipitation of the chloride. Calculate the percentages of Na and K.

Ans. 4.48 per cent K; 0.57 per cent Na.

4. If the mixture of NaCl and KCl in Problem 3 had been converted to mixed sulfates by treatment with H_2SO_4, what weight of each sulfate would have been obtained? *Ans.* 0.1997 g K_2SO_4; 0.0354 g Na_2SO_4.

5. If a mixture of AgBr and AgCl contains 65 per cent Ag, what is the percentage of Cl? *Ans.* 10.49 per cent.

6. If x = weight of Ca, y = weight of Sr, a = weight of mixed CaO and SrO, and b = weight of mixed $CaSO_4$, calculate the factors for x and y in terms of a and b. *Ans.* $x = 1.1066\ b - 1.9717\ a$; $y = 3.1785\ a - 1.3093\ b$.

7. A mixture of calcium and barium oxides weighed 2.210 g. This mixture yielded 5.020 g of mixed sulfates. Calculate the weight of each oxide in the original mixture. *Ans.* 0.3814 g BaO; 1.8286 g CaO.

8. A sample of 1.800 g gave a precipitate of 1.200 g of mixed AgCl and AgI. Following chlorination of the mixed salts, the AgCl remaining weighed 0.9750 g. Calculate the percentages of Cl and I.

Ans. 8.55 per cent Cl; 17.34 per cent I.

9. A sample of 2.000 g gave a precipitate of 0.9500 g of mixed AgBr and AgI. Following chlorination, the AgCl weighed 0.6300 g. Calculate the percentages of Br and I. *Ans.* 6.98 per cent Br; 16.81 per cent I.

10. A sample of 1.0000 g of limestone gave 20 mg of mixed Al_2O_3 and Fe_2O_3. The Fe_2O_3 was dissolved, the Fe converted to a colored complex, diluted to 100 ml, and measured colorimetrically. If a 40-mm thickness of unknown solution color-matched 32 mm of an iron solution containing 0.000050 g Fe/ml, calculate the percentage of Al. *Ans.* 0.76 per cent.

COLORIMETRIC METHODS [40]

The student should review the definitions for relevant terms, particularly transmittance T, transmittancy T_s, transmittance of unit thickness t, per cent transmittance 100 T (or transmittancy T_s) absorbance A, absorbancy A_s, absorbance index a, molar absorbancy index a_M, cell thickness b, and the absorption laws. Most important is an understanding of the relationships

$$\begin{aligned} I/I_0 &= T \\ \log I_0/I &= \log 1/T = A = abc \\ T &= t^b \text{ (Bouguer's law)} \\ &= t^c \text{ (Beer's law)} \end{aligned}$$

Methods of plotting and using such absorptimetric data should be reviewed. Chapter 17 covers principles of using a balancing comparimeter

[40] See Chapter 17 for a general discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 259.

and different kinds of photometers; Chapter 29 gives specific applications.

1. The absorbance of a glass at 520 mμ is 1.2 and the per cent transmittance at 600 mμ is 50. Calculate the per cent transmittance at 520 mμ and the absorbance at 600 mμ. *Ans.* 6.3 per cent; 0.30.

2. A purple plastic has the following per cent transmittances at the respective wave lengths: 85.0 (400); 60.0 (450); 18.0 (500); 20.0 (550); 60.0 (600); 85.0 (650); 100 (700). Calculate for each per cent transmittance T the respective absorbance A and the log absorbance, log A. Construct a graph showing these data in the form of spectrophotometric curves. Plot as the abscissa the wave length and as the three ordinates the per cent transmittance, the absorbance, and the log absorbance.

3. A transmittancy of 0.40 was found for a solution containing 2 mg of iron per liter in the form of the ferrous-1,10-phenanthroline complex, $Fe(C_{12}H_8N_2)_3^{+2}$. The cell thickness was 1 cm. Calculate the absorbancy index a for this solution, and also the molar absorbancy index a_M, for a similar solution having a concentration of 1 M. *Ans.* $a = 199$; $a_M = 11{,}110$.

4. The transmittance at 500 mμ of a glass 2 cm thick is 60 per cent; calculate the value for this glass for a thickness of 5 cm. *Ans.* 27.9 per cent.

5. The absorbancy of a solution containing 5.0 mg per liter is 0.40 at 510 mμ. Assuming that the solution conforms to Beer's law, for what concentration would the absorbancy be 1.20? *Ans.* 0.87 mg per liter.

6. A solution containing 1.0 mg of iron per liter, as the ferrous-1,10-phenanthroline complex, absorbs 65 per cent of the light at 510 mμ in a 1-cm cell thickness. What would be the concentration of a solution which absorbs (at the same wave length) 30 per cent of the light in a 2-cm cell?

Ans. 0.169 mg per liter.

7. At 505 mμ a series of solutions of the cobaltous-2,2′,2″-terpyridine complex gave the following per cent transmittancies in a 1-cm cell for the respective concentrations (mg/liter): 90.0 (3); 77.0 (5); 56.0 (10); 33.0 (20); 20.0 (30); 7.5 (50): Suggest two ways of plotting the data to test for conformity of the system to Beer's law. Does it conform?

8. In a balancing comparimeter a solution of $KMnO_4$, 5.0 cm thick and containing 2.00 mg of Mn/liter, visually matched an unknown solution 8.0 cm thick. If the solution conforms to Beer's law, what was the concentration of Mn in the unknown? *Ans.* 1.25 mg/liter.

9. Assume the molar absorbancy index a_M of ferrous-2,2′-bipyridine is 10,500 (cell = 1 cm thick). If the transmittancy of an unknown solution of the same thickness is 47.5 per cent, what is the concentration in mg/liter?

Ans. 1.73 mg/liter.

10. A sample of 0.2000 g of a cobalt alloy was dissolved, complexed with 2,2′,2″-terpyridine, and diluted to 250 ml. The transmittancy of the solution at 505 mμ was 50.0 per cent in a 1-cm cell. Using the data of Problem 7 for a calibration curve, calculate the percentage of cobalt in the alloy.

Ans. 1.50 per cent.

MISCELLANEOUS PROBLEMS INVOLVING EQUILIBRIA

Various kinds of equilibrium problems have been basic for some decades in teaching the foundation of inorganic qualititative analysis. The few of this type included here were selected merely for review, and no explanation is given for making such calculations. If necessary, the student should review the topics concerned. The problems have been grouped roughly for convenience.

Ionic Equilibria[41]

Under the heading of ionic equilibria are included topics such as solubility, solubility product, dissociation, ionization, hydrolysis, pH, buffers, and complexation.

1. If a solution of NH_4OH is 2.5 per cent ionized, and the ionization constant is 1.75×10^{-5}, what is the molarity of the solution?

Ans. 0.0275 *M*.

2. What is the hydrogen ion concentration of a solution 0.1 *N* in $HC_2H_3O_2$ if the ionization constant of the acid is 1.8×10^{-5}?

Ans. 1.34×10^{-3} *M*.

3. Calculate the concentration of hydroxyl ions in a 0.1 *M* solution of NH_4OH which contains 0.5 mole of NH_4Cl per liter (assume 85 per cent ionization). *Ans.* 4.12×10^{-6} *M*.

4. Calculate the approximate hydrogen ion concentration of a solution of 500 ml of 0.1 *N* $HC_2H_3O_2$ to which 10 g of $NaC_2H_3O_2$ is added. Assume that the acid is ionized 1.35 per cent and the salt 80 per cent.

Ans. 9.16×10^{-6} *M*.

5. For each of the following experiments, state whether the *p*H of the *final* solution is above 7, equal to 7, or less than 7:

(a) 50 ml of 0.001 *M* HCl is added to 50 ml of 0.001 *M* NaOH.
(b) 50 ml of 0.1 *M* $HC_2H_3O_2$ is added to 50 ml of 0.09 *M* NaOH.
(c) 25 ml of 0.1 *M* NH_4OH is added to 50 ml of 0.05 *M* HCl.
(d) 25 ml of 0.1 *M* HCl is added to 25 ml of 0.1 *M* Na_2CO_3.

Ans. (a) 7; (b) <7; (c) <7; (d) >7.

6. The ionization constant K_b of a base BOH is 2×10^{-6}. Calculate the *p*H of the solution obtained on adding to a 0.2 *M* solution of BOH an equal volume of 0.1 *M* HCl. *Ans.* 5.7.

7. 50 ml of 0.08 *M* NaOH is added to 50 ml of 0.10 *M* solution of a weak acid. The *p*H of the resulting solution is 8.0. Calculate the K_a for the weak acid. *Ans.* 4×10^{-8}.

8. Suppose that 50 ml of 0.1 *M* formic acid ($K_a = 2 \times 10^{-4}$) is titrated

[41] See Chapters 8, 13, and 28 for a general discussion of the phenomena involved; also see Hamilton and Simpson, *op. cit.*, pp. 41-63.

with 0.1 *M* NaOH. What will be the *p*H of the solution (to the nearest 0.1 unit) after addition of 0.0, 50, and 55 ml of the titrant base?

Ans. 2.35; 8.2; 11.7.

9. Calculate the per cent of acid neutralized when 40 ml of 0.1 *N* $HC_2H_3O_2$ has been treated with 0.1 *N* NaOH until a *p*H of 7 is reached.

Ans. 99.44 per cent.

10. Calculate the per cent of carbonate neutralized when 40 ml of 0.1 *N* Na_2CO_3 has been treated with 0.1 *N* HCl until a *p*H of 7 has been reached.

Ans. 62.5 per cent.

11. Calculate the respective solubility products for the salts having the solubilities given, in g/liter: AgCl = 1.5×10^{-3}; $CaC_2O_4 = 8 \times 10^{-3}$; $MgNH_4PO_4 = 0.0086$; $Ag_2CrO_4 = 2.5 \times 10^{-2}$; $Fe(OH)_3 = 4.8 \times 10^{-8}$.

Ans. AgCl = 1.10×10^{-10}; $CaC_2O_4 = 3.90 \times 10^{-9}$; $MgNH_4PO_4 = 2.46 \times 10^{-13}$; $Ag_2CrO_4 = 1.71 \times 10^{-12}$; $Fe(OH)_3 = 1.10 \times 10^{-36}$.

12. Calculate the respective solubilities in g/liter for the salts having the solubility products given: $Ag_3PO_4 = 1.8 \times 10^{-18}$; $Mg(OH)_2 = 3.5 \times 10^{-11}$; AgBr = 3.4×10^{-13}; $Hg_2Cl_2 = 2.1 \times 10^{-18}$; $SrSO_4 = 3.6 \times 10^{-7}$.

Ans. $Ag_3PO_4 = 6.7 \times 10^{-3}$ g; $Mg(OH)_2 = 0.01202$ g; AgBr = 1.095×10^{-4} g; $Hg_2Cl_2 = 9.0 \times 10^{-3}$ g; $SrSO_4 = 0.1102$ g.

13. If the solubility product of SrF_2 is 2.5×10^{-8}, how many milligrams will dissolve in 200 ml of water? *Ans.* 46.3 mg/200 ml.

14. What is the solubility product of $Pb_3(PO_4)_2$ if 200 ml of a saturated solution contains 2×10^{-5} g of lead ions? *Ans.* 1.16×10^{-32}.

15. A solution contains 5 mg of K_2CrO_4 in 100 ml. If the solubility product of Ag_2CrO_4 is 1.7×10^{-12}, how many grams of $AgNO_3$ would be required to cause a precipitate to form? *Ans.* 0.00138 g.

16. If the solubility product of $Fe(OH)_2$ is 2×10^{-14}, and if the ionization constant of NH_4OH is 1.75×10^{-5}, show whether a precipitate would form in a solution 0.05 *M* in NH_4^+ ions, 0.01 *M* in Fe^{++} ions, and 0.01 *M* in NH_4OH.

Ans. Will form.

17. How much NH_4Cl (in terms of molarity of final solution) must be added to a 0.01 *M* solution of Mg^{++} ions to prevent precipitation of $Mg(OH)_2$ if the solution must be 0.2 *M* in NH_4OH? (K_{sp} $Mg(OH)_2 = 3.5 \times 10^{-11}$; $K_b NH_4OH = 1.8 \times 10^{-5}$) *Ans.* 0.0608 *M*.

18. The solubility of AgBr in water is 0.11 mg/liter. Calculate the solubility in 0.1 *M* KBr in mg/liter. *Ans.* 6.44×10^{-8} mg.

19. A solution of 250 ml that is 0.01 *M* in a tervalent metal and 1.0 *M* in hydrogen ion, is saturated with H_2S. When precipitation is completed, 15 millimoles of the metal remain in solution. Calculate the approximate solubility product of the metal sulfide. (Solubility of H_2S is 0.10 *M*; ionization constants for H_2S are 9.1×10^{-8} and 1.2×10^{-15}). *Ans.* 4.7×10^{-72}.

20. H_2S was passed into a 0.01 *M* solution of $CuCl_2$ until equilibrium was reached. The final concentration of the dissolved gas was 0.1 *M*. The solubility product of CuS is 10^{-42} and the ionization constants of H_2S are given

in Problem 19. Calculate the final concentrations of H^+, HS^-, S^{-2}, and Cu^{+2}. *Ans.* $[H^+] = 0.02$; $[HS^-] = 4.55 \times 10^{-7}$; $[S^{-2}] = 2.73 \times 10^{-20}$; $[Cu^{+2}] = 3.7 \times 10^{-23}$ *M*.

21. The K_{sp} of AgCl is 1.0×10^{-10}. What is the maximum volume of water that can be used to wash 0.5000 g of AgCl without having the solubility loss on washing exceed 0.1 per cent? *Ans.* 348.9 ml.

22. The K_{sp} of $AgC_2H_3O_2$ is 4.4×10^{-3} and the ionization constant of acetic acid is 1.8×10^{-5}. Calculate the molar solubility of $AgC_2H_3O_2$ in a solution in which the $[H^+]$ is 10^{-5}. *Ans.* 8.27×10^{-2} *M*.

23. The solubility of $BaSO_4$ in water is 1.0×10^{-5} mole/liter. Calculate the molar concentration of Ba^{+2} ion in 2 *M* HCl. The second ionization constant of H_2SO_4 is 1.2×10^{-2}. *Ans.* 1.29×10^{-4} *M*.

24. The solubility product of $Cu(OH)_2$ is 1.0×10^{-20} and that of $Fe(OH)_3$ is 1.0×10^{-36}. A solution is originally 0.1 *M* in both Fe^{+3} and Cu^{+2} ions. Between what limits must the molar concentration of OH^- ion be maintained to precipitate the iron completely as $Fe(OH)_3$ and not precipitate any of the copper? (This means to reduce the Fe^{+3} ion concentration to 10^{-6} *M*.) *Ans.* Between 1.0×10^{-10} and 3.2×10^{-10} *M*.

25. Compute the molar concentrations of Ag^+, Br^-, and SCN^- ions in a solution prepared by shaking an excess of both AgBr and AgSCN with water until equilibrium is reached. (K_{sp}: AgBr $= 3.3 \times 10^{-13}$; AgSCN $= 1.0 \times 10^{-12}$.)

Ans. $Ag^+ = 1.19 \times 10^{-6}$; $Br^- = 2.86 \times 10^{-7}$; $SCN^- = 8.4 \times 10^{-7}$ *M*.

26. If the K_{sp} of AgSCN is 1.0×10^{-12}, what is its molar solubility in (a) 1.0×10^{-6} *M* $AgNO_3$, and (b) 1.0 *M* NH_4OH? (The dissociation constant of the silver complex is 6.8×10^{-8}.)

Ans. (a) 6.2×10^{-7}; (b) 3.8×10^{-3} *M*.

Redox Equilibria[42]

Problems involving the relative concentrations of reactants in redox titrations at various values of potential during the course of the titration may be solved by application of the Nernst equation to the sysems involved. Naturally, the reverse situation may be handled similarly. It should be kept in mind that at every stage of a redox titration there are two redox systems in equilibrium

$$ox_1 + red_2 \rightarrow red_1 + ox_2$$

and that the potentials of the two half-cell systems involved, as calculated by the Nernst equation, are equal. The equilibrium constant and potential at the equivalence point for such a process may be calculated from the standard potentials of the two half-cells concerned.

[42] See Chapters 14 and 26 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 236.

1. Calculate the electrode potential at which 0.12 *M* $Ce(SO_4)_2$ is one-fourth reduced to $Ce_2(SO_4)_3$ by the addition of 0.12 *M* $FeSO_4$. ($[H^+] = 1.0\ M$; $E^0 = 1.45$ volts for Ce^{+4}/Ce^{+3} in sulfate solution.) *Ans.* −1.47 volts.

2. If 0.1 *M* $Fe_2(SO_4)_3$ is titrated with 0.1 *M* $CrSO_4$ in a nonoxidizing atmosphere according to the equation

$$Fe^{+3} + Cr^{+2} \rightarrow Cr^{+3} + Fe^{+2}$$

calculate the oxidation potential of the solution after the following percentages of the necessary equivalent amount of chromous solution have been added: 9, 50, 91, 99, 100, 101. See Table 14.1 (page 223) for E^0 values for the Fe^{+3}/Fe^{+2} and the Cr^{+3}/Cr^{+2} systems.

Ans. 9 = −0.83; 50 = −0.77; 91 = −0.71; 99 = −0.65; 100 = −0.18; 101 = +0.29 volts.

3. If the titration of 0.1 *N* $Ce(SO_4)_2$ with 0.1 *N* $FeSO_4$ is continued at 25° until a potential of 1.263 volts is reached, calculate (a) the ratio of the concentrations of Ce^{+4} to Ce^{+3}, and (b) the actual concentrations of Ce^{+4} and Ce^{+3} ions. Assume complete ionization in all cases. See Table 14.1 (page 223) for E^0 values for the Ce^{+4}/Ce^{+3} and the Fe^{+3}/Fe^{+2} systems.

Ans. (a) 7.78×10^{-4}; (b) $Ce^{+4} = 0.00038$ and $Ce^{+3} = 0.4996\ M$.

4. Calculate the equilibrium constant for the following reaction:

$$H_3AsO_4 + 2\ H^+ + 3\ I^- \rightarrow HAsO_2 + I_3^- + 2\ H_2O$$

The half-cell reactions are

$$HAsO_2 + 2\ H_2O \rightleftharpoons H_3AsO_4 + 2\ H^+ + 2\ e \qquad E^0 = -0.559 \text{ volt}$$
$$3\ I^- \rightleftharpoons I_3^- + 2\ e \qquad E^0 = -0.535 \text{ volt}$$

Ans. 6.4.

5. Calculate the approximate amount or fraction of the arsenate in the previous problem that is unreduced in a solution 0.4 *M* in I^-, 3 *M* in H^+, and originally 0.02 *M* in arsenate. *Ans.* 0.54 per cent.

6. In the titration of 50 ml of 0.1 *M* Fe^{+2} with 0.02 *M* $K_2Cr_2O_7$, the analyst forgets to add H_3PO_4. The diphenylaminesulfonate indicator changes color at −0.84 volts. Calculate the titration error in per cent with proper sign.

$$Fe^{+2} \rightleftharpoons Fe^{+3} + e \qquad E^0 = -0.77 \text{ volt}$$
$$2\ Cr^{+3} + 7\ H_2O \rightleftharpoons Cr_2O_7^{-2} + 14\ H^+ + 6\ e \qquad E^0 = -1.36 \text{ volt}$$

Ans. −2.13 per cent.

7. Suppose that 50 ml of a 0.01 *M* solution of Fe^{+2} ion in 1 *N* H_2SO_4 is titrated with 0.01 *M* $Ce(SO_4)_2$, using diphenylaminesulfonate as indicator, and that the end point is observed when 50 per cent of the indicator has been oxidized. The standard potential of the ferric-ferrous system is −0.77 volt, that of the indicator system is −0.84 volt, and that of the ceric-cerous system is −1.45 volts. (a) What fraction or percentage of the ferrous ion will have been oxidized when the end point is observed? (b) How can the conditions of titration be changed so that the observed end point with diphenylamine

sulfonate will more nearly coincide with the equivalence point? (c) What should be the oxidation potential of an indicator for this titration in order that the observed end point will coincide with the equivalence point?

Ans. (a) 93.4 per cent; (b) add H_3PO_4; (c) -1.11 volts.

Electrometry[43]

The few problems included here deal with the use of glass, hydrogen, and quinhydrone electrodes for the determination of *p*H values and the concentration of hydrogen ions.

1. If the hydrogen ion concentration of a solution is 3.5×10^{-7} *M*, what is the *p*H? What is the hydrogen ion concentration of a solution the *p*H of which is 8.34? *Ans.* *p*H = 6.46; $[H^+] = 4.57 \times 10^{-9}$ *M*.

2. If the potential of a hydrogen electrode in 0.1 *N* HCl, measured against a saturated calomel electrode (−0.244) is 0.310 volt, what is the *p*H of the acid? *Ans.* *p*H = 1.12.

3. Calculate the *p*H of a buffer solution, containing equal volumes of 0.2 *M* $NaC_2H_3O_2$ and 0.2 *M* $HC_2H_3O_2$, if at 18° a quinhydrone electrode gave an emf of 0.100 volt against a 0.1 *N* calomel electrode. *Ans.* *p*H = 4.58.

4. If a glass electrode, measured against a reference electrode, gave a potential of 1.495 volts in 0.1 *M* HCl and 1.273 volts in an unknown solution, calculate the latter's *p*H (*p*H of acid = 1.03). *Ans.* *p*H = 4.78.

5. If a hydrogen electrode, measured against a normal calomel electrode gave a potential of 0.660 volt in a solution of 0.05 *M* $NH_4C_2H_3O_2$, and 0.486 volt for an unknown solution, calculate the difference in *p*H of the two solutions and the *p*H of the unknown (assume equal ionization constants for $HC_2H_3O_2$ and NH_4OH). *Ans.* Difference in *p*H = 2.95; *p*H of unknown = 3.47.

6. If a hydrogen electrode, measured against a normal calomel electrode at 25°, gave a potential of 500 millivolts, what was the hydrogen ion concentration and *p*H of the solution?

Ans. $[H^+] = 1.99 \times 10^{-4}$ *M*; *p*H = 3.67.

7. It is desired to stop a potentiometric titration of a strong acid with a strong base at the point of stoichiometric neutrality (*p*H 7). If the titration is carried out at 25° with a normal calomel and a quinhydrone electrode what should be the reading of the potentiometer in millivolts at the equivalence point? *Ans.* 4.5 millivolts.

8. For a 0.05 *M* solution of $KHC_8H_4O_4$ an emf of 0.5689 volt was obtained at 20° with hydrogen and 0.1 *N* calomel electrodes. What is the *p*H of the phthalate solution? *Ans.* 3.95.

[43] See Chapters 18 and 30 for a discussion of this subject; also see Hamilton and Simpson, *op. cit.*, p. 233.

Electrodeposition[44]

Ohm's law and the potential relationships discussed in Chapter 9 are usually sufficient for calculations of potentials. Common sense plus an attempt to get a physical interpretation of what is occurring seem to help in attacking problems on overvoltage. The concentrations of given constituents at a specified potential, or the reverse situation, can usually be handled by use of the Nernst equation.

1. Calculate the theoretical back-emf for a solution of 200 ml containing 0.2 g of copper and 0.01 *M* in H_2SO_4. What would the value be for 1.0 *M* acid? If the acidity were maintained at 0.1 *M*, what would be the back-emf when the concentration of Cu^{+2} ions decreased to 10^{-4} *M*?

Ans. 0.84 volt; 0.97 volt; 0.97 volt.

2. If oxygen is liberated at the anode when silver is deposited from the complex cyanide $Ag(CN)_2^-$, what would be the theoretical back-emf when only 0.1 mg of silver remained in a solution of 100 ml? *Ans.* 1.55 volts.

3. A sample of 0.3 g of an alloy containing 90 per cent silver and 10 per cent copper was dissolved and diluted to 200 ml. Assuming the solution to be 0.1 *M* in HNO_3, what will happen if one electrolyzes the solution at 1 volt (Disregard internal resistance of the solution and overvoltage)?

Ans. Both metals will deposit ($E_{Ag} = 0.48$ volt and $E_{Cu} = 0.90$ volt).

4. A sample of 0.2 g of an alloy consisting of equal parts of Ni and Cd was dissolved in H_2SO_4 and diluted to 250 ml. If the acid was 0.1 *N*, show what the concentration of Ni will be when the Cd begins to deposit.

Ans. $[Ni^{+2}] = 5.5 \times 10^{-9}$ *M*.

[44] See Chapters 9 and 28 for a discussion of the subject; also see Hamilton and Simpson, *op. cit.*, p. 114.

APPENDIX

FORMULA WEIGHTS

The formula weights used in the problems used in this book are listed below. To obtain the formula weight for a hydrate of a given compound, it is necessary to add to the weight of the anhydrous compound the value for the number of water molecules involved.

Formula	*Weight*	*Formula*	*Weight*	*Formula*	*Weight*
$AgBr$	187.80	$FeSO_4 \cdot (NH_4)_2SO_4$	284.06	KHC_2O_4	128.12
$AgCl$	143.34	$Fe_2(SO_4)_3$	399.91	$KHC_2O_4 \cdot H_2C_2O_4$	218.16
$AgCN$	133.90	H_3AsO_3	125.93	KH_2PO_4	136.09
$Ag(C_2H_3O_2)$	166.92	H_3AsO_4	161.93	$KHSO_4$	136.17
Ag_2CrO_4	331.77	H_3BO_3	61.84	KI	166.02
AgI	234.80	$HCOOH$	46.03	KIO_3	214.02
$AgNO_3$	169.89	$HC_2H_3O_2$	60.05	$KIO_3 \cdot HIO_3$	389.95
Ag_3PO_4	418.62	H_2CO_3	62.03	KIO_4	230.02
$AgSCN$	165.97	$H_2C_2O_4$	90.04	$KMnO_4$	158.03
Al_2O_3	101.94	$H_2Ce(SO_4)_3$	430.34	$KSCN$	97.18
As_2O_3	197.82	HCl	36.46	K_2O	94.19
B_2O_3	69.64	$HClO_4$	100.46	KOH	56.10
$BaCO_3$	197.37	HNO_3	63.02	$KOOC_{16}H_{31}$	294.51
$BaCl_2$	208.27	H_2O	18.02	K_2PtCl_6	486.16
BaO	153.36	$2\ H_2O$	36.03	K_2SO_4	174.26
$Ba(OH)_2$	171.38	$3\ H_2O$	54.05	$LiCl$	42.40
$BaSO_4$	233.43	$4\ H_2O$	72.06	Li_2CO_3	73.89
$(CH_3CO)_2O$	102.09	$5\ H_2O$	90.08	$LiHCO_3$	67.96
CO_2	44.01	$6\ H_2O$	108.10	Li_2O	29.88
$CaCO_3$	100.09	$7\ H_2O$	126.11	$LiOH$	23.95
CaC_2O_4	128.10	$8\ H_2O$	144.13	Li_3PO_4	115.80
$CaCl_2$	110.99	$9\ H_2O$	162.14	$Mg_2As_2O_7$	310.46
$Ca(HCO_3)_2$	162.12	H_2O_2	34.02	$MgCO_3$	84.33
$CaHPO_4$	136.07	$HO(NH_2)SO_2$	97.10	$MgNH_4PO_4$	137.34
CaO	56.08	H_3PO_4	98.00	MgO	40.32
$Ca(OH)_2$	74.10	H_2S	34.08	$Mg(OH)_2$	58.34
$CaSO_4$	136.15	H_2SO_3	82.08	$Mg_2P_2O_7$	222.60
CeO_2	172.13	H_2SO_4	98.08	MnO_2	86.93

FORMULA WEIGHTS (Continued)

Formula	*Weight*	*Formula*	*Weight*	*Formula*	*Weight*
$Ce(SO_4)_2$	332.25	H_2SiF_6	144.08	Mn_3O_4	228.79
$Ce_2(SO_4)_3$	568.46	H_2SnCl_4	262.54	$Mn_2P_2O_7$	283.82
$CrCl_2$	122.92	H_3VO_4	117.97	MoO_3	143.95
$CrSO_4$	148.08	H_2WO_4	249.94	NH_3	17.03
$CuCl_2$	134.45	Hg_2Cl_2	472.13	NH_4	18.04
CuSCN	121.62	K_3AsO_4	256.20	$(NH_4)_2C_2O_4$	124.10
$Cu(NO_3)_2$	187.56	KBF_4	125.92	$(NH_4)_2Ce(NO_3)_6$	548.26
CuO	79.54	KBr	119.02	NH_4Cl	53.50
$Cu(OH)_2$	97.56	$KBrO_3$	167.01	$(NH_4)_2HPO_4$	132.07
CuS	95.61	KCl	74.55	NH_4OH	35.05
$CuSO_4$	159.61	$KClO_4$	138.55	$(NH_4)_2MoO_4$	196.03
$FeCl_2$	126.76	KCN	65.11	$(NH_4)_3P(Mo_3O_{10})_4$	1876.50
$FeCl_3$	162.22	K_2CO_3	138.20	$(NH_4)_2SO_4$	132.15
FeO	71.85	K_2CrO_4	194.20	N_2O_5	108.02
Fe_2O_3	159.70	$K_2Cr_2O_7$	294.21	Na_3AsO_3	191.90
Fe_3O_4	231.55	$K_3Fe(CN)_6$	329.25	$Na_2B_4O_7$	201.27
$Fe(OH)_3$	106.87	$K_4Fe(CN)_6$	368.34	$NaC_2H_3O_2$	82.04
$FeSO_4$	151.92	$KHC_8H_4O_4$	204.22	Na_2CO_3	106.00
$Na_2C_2O_4$	134.01	$PbMoO_4$	367.16	SrO	103.63
Na_2CS_3	154.20	PbO	223.21	$SrSO_4$	183.70
NaCl	58.45	PbO_2	239.21	$TiCl_3$	154.27
$NaHCO_3$	84.02	Pb_3O_4	685.63	TiO_2	79.80
Na_2O	61.99	$Pb_3(PO_4)_2$	811.59	UCl_4	379.90
NaOH	40.00	$PbSO_4$	303.28	$UO_2(C_2H_3O_2)_2$	388.16
Na_2S	78.06	Sb_2O_4	307.52	U_3O_8	842.21
Na_2SO_4	142.06	SiO_2	60.06	V_2O_5	181.90
$Na_2S_2O_3$	158 13	SnO_2	150.70	WO_3	231.92
$Ni(C_4H_7O_2N_2)_2$	288.91	SO_2	64.07	$ZnNH_4PO_4$	178.40
OH	17.01	SO_3	80.07	ZnO	81.38
P_2O_5	141.96	SO_4	96.07	$Zn_2P_2O_7$	304.72
$PbCl_2$	278.12	$SrCO_3$	147.64		
$PbCrO_4$	323 22	SrF_2	125.63		

COMPOSITION DATA FOR CONCENTRATED ACIDS AND AMMONIA

Substance	*Specific Gravity*	*Weight* (per cent)	*Molarity*
Acetic acid	1.05	99.5	17.4
Ammonium hydroxide	0.90	27 (NH_3)	14.3
Hydrochloric acid	1.18	37	12.0
Hydrofluoric acid	1.15	48	27.6
Nitric acid	1.41	70	15.7
Perchloric acid	1.67	70	11.6
Phosphoric acid	1.69	85	14.7
Sulfuric acid	1.83	95.5	17.8

SPECIFIC GRAVITY OF SELECTED MATERIALS

Aluminum	2.70	*Primary standards*	
Brass, ordinary	8.4	Arsenious oxide	3.74
weights	8.0	Iodine	4.93
Copper	8.94	Potassium dichromate	2.69
Gold	19.3	Potassium hydrogen phthalate	1.63
Platinum	21.4	Sodium borate decahydrate	1.73
Tantalum	16.6	Sodium carbonate	2.53
Porcelain	2.4	Sodium oxalate	2.27
Glass, white	2.6	*Residues*	
Silica (quartz)	2.65	Aluminum oxide	4.00
		Barium sulfate	4.50
		Calcium oxide	3.32
		Ferric oxide	5.12
		Lead sulfate	6.2
		Magnesium oxide	3.65
		Magnesium pyrophosphate	2.60
		Silver chloride	5.56
		Tin oxide	7.0
		Zinc pyrophosphate	3.75

WEIGHT OF A LITER OF DRY AIR
(in grams)

Temperature (°C)	*Barometric Pressure* (mm)				
	720	730	740	750	760
15	1.161	1.178	1.194	1.210	1.226
16	.157	.174	.190	.206	.222
17	.153	.169	.185	.201	.218
18	.149	.165	.181	.197	.213
19	.146	.161	.177	.193	.209
20	.142	.157	.173	.189	.205
21	.138	.154	.169	.185	.201
22	.134	.150	.165	.181	.197
23	.130	.146	.161	.177	.193
24	.126	.142	.158	.173	.189
25	.122	.138	.154	.169	.185
26	.119	.134	.150	.165	.181
27	.115	.130	.146	.161	.177
28	.111	.127	.142	.158	.173
29	.108	.123	.138	.154	.169
30	.104	.119	.135	.150	.165
31	.101	.116	132	.147	.161
32	.098	.112	.128	.143	.157
33	.094	.108	.124	.139	.153
34	.091	.107	.121	.136	.150
35	.087	.103	.117	.132	.146

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