QUANTITATIVE

CHEMICAL ANALYSIS

TALBOT

AN INTRODUCTORY COURSE

OF

QUANTITATIVE
CHEMICAL ANALYSIS

WITH

EXPLANATORY NOTES

AND

STOICHIOMETRICAL PROBLEMS

BY

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PREFACE

THIS Introductory Course of Quantitative Analysis has been prepared to meet the needs of students who are just entering upon the subject, after a course of qualitative analysis. It is primarily intended to enable the student to work successfully and intelligently, without the necessity for a larger measure of personal assistance and supervision than can reasonably be given to each member of a large class. To this end the directions are given in such detail that there is very little opportunity for the student to go astray; but the manual is not, the author believes, on this account less adapted for use with small classes, where the instructor, by greater personal influence, can stimulate independent thought on the part of the pupil.

The method of presentation of the subject is that suggested by Professor A. A. Noyes' excellent manual of Qualitative Analysis. For each analysis the procedure is given in considerable detail, and this is accompanied by explanatory notes, which are believed to be sufficiently expanded to enable the student to understand fully the underlying reason for each step prescribed. The use of the book should nevertheless be supplemented by classroom instruction, mainly of the character of recitations, and the student should be taught to consult the larger works, such as those of Fresenius, Treadwell-Hall, and Sutton. The general directions of Part I are intended to emphasize those matters upon which the beginner in quantitative analysis must bestow special care, and to offer some helpful suggestions. The student can hardly be expected to appreciate the force of all the statements contained in these directions, or, indeed, to retain them all in the memory after a single reading; but the instructor, by frequent reference to special paragraphs as suitable occasion presents itself, can soon render them familiar to the student.

The analyses selected for practice are those comprised in the course of "preliminary quantitative analysis" at the Massachusetts Institute of Technology, and have been chosen, after an experience of some years, as affording the best preparation for more advanced work, and as satisfactory types of gravimetric and volumetric methods. From the latter point of view, they

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. also seem to furnish the best insight into quantitative analysis for those students who can devote but a limited time to the subject, and who may never extend their study beyond the field covered by this manual. The author has had opportunity to test the efficiency of the course for use with such students, and has found the results satisfactory.

In place of the usual custom of selecting simple salts as material for preliminary practice, it has been found advantageous to substitute, in most instances, approximately pure samples of appropriate minerals or industrial products. The difficulties are not greatly enhanced. while the student gains in practical experience.

It has been found expedient with large classes to allow the whole class to work simultaneously upon the same procedure (for example, that for the determination of chlorine in sodium chloride), since classroom instruction can then be made more effective. Each individual is, however, permitted to work as rapidly as his capacity admits; and to such students as exhibit unusual facility in manipulation extra analyses are assigned.

The author has been unable to find any work in which such stoichiometrical problems as are constantly met with in the experience of an analyst are dealt with in such detail as to enable the student to understand fully the underlying principles. A chapter has therefore been added in which such problems are presented and the solutions of certain typical cases are explained. A table of atomic weights and a table of four-place logarithms are appended for convenience.

The analytical procedures described in the following pages have been selected chiefly with reference to their usefulness in teaching the subject, and with the purpose of affording as wide a variety of processes as is practicable within an introductory course of this character. The scope of the manual precludes any extended attempt to indicate alternative procedures, except through general references to larger works on analytical chemistry. The author is indebted to the standard works for many suggestions for which it is impracticable to make specific acknowledgment; but no considerable credit is claimed by him for originality of procedure.

In the present (the fifth) edition, the entire text has been revised and reset, and it has been largely rewritten. Several of the pro-

cedures have been slightly modified to bring them into accord with the results of recently published investigations and with experience gained in the laboratory, and a complete analysis of a limestone replaces the partial analysis of dolomite. The number of problems has been increased from forty-five to seventy, the old ones being nearly all retained, but these have been recalculated, using the latest values for atomic weights.

The chief innovation in the present edition is the incorporation of statements regarding the important ionic changes involved into the notes which follow each analytical procedure. It is to be remembered that experimental data are not yet at hand which permit of exact statements in all of these cases. The statements made must, therefore, be regarded as merely indicative of the general character of the ionic changes, and as subject to modification as our knowledge broadens. Although the electrolytic dissociation theory is now quite generally made a part of the instruction in inorganic chemistry which precedes that in analytical chemistry, it has seemed wise, for convenience of reference, to retain in the Appendix a brief statement of the theory itself and some illustrations of its application in typical cases. The instructor will find it desirable to present much in the way of additional detail and illustration, and the student should be encouraged to read other and more extended treatises on this subject.

The author wishes to renew his expressions of appreciation of the kindly reception accorded the earlier editions of this manual. He has received helpful suggestions from so many of his colleagues within the Institute, and friends elsewhere, that his sense of obligation must be expressed to them collectively; but it is none the less sincere on that account.

HENRY P. TALBOT.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
        March, 1908.
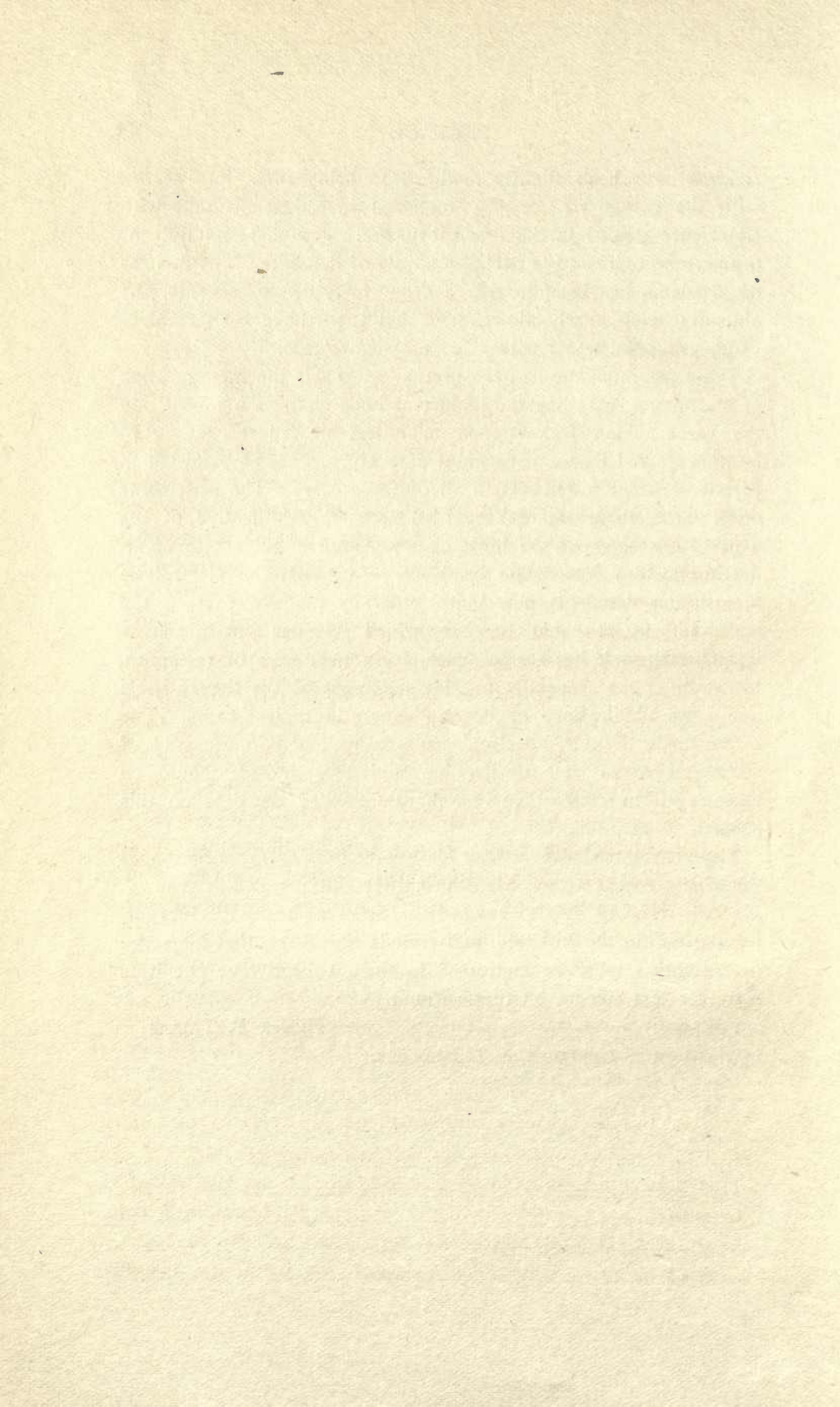
PART I

INTRODUCTION

A COMPLETE chemical analysis of a body of unknown composition involves the recognition of its component parts by the methods of *qualitative analysis,* and the determination of the proportions in which these components are present by the processes of *quantitative analysis.* The qualitative examination is generally indispensable, if intelligent and proper provisions are to be made for the separation of the various constituents under such conditions as shall insure accurate quantitative estimations.

It is assumed that the operations of *qualitative* analysis are familiar to the student, who will find that the reactions made use of in *quantitative* processes are not infrequently those employed for the qualitative detection of the same element; but it should be noted that the conditions must now be regulated with greater care, and in such a manner as to insure the most complete separations possible. For example, in the qualitative detection of sulphates by precipitation as barium sulphate from acid solution, it is not necessary, in most instances, to regard the solubility of the sulphate in hydrochloric acid, while in the quantitative determination of sulphates by this reaction this solubility becomes an important consideration. The operations of qualitative analysis are, therefore, the more accurate the nearer they are made to conform to quantitative conditions.

The methods of quantitative analysis are subdivided, according to their nature, into those of *gravimetric* and *volumetric* analysis. In *gravimetric* processes the constituent to be determined is isolated in the form of some compound possessing a well-established and definite composition, which can be readily and completely separated by filtration, and weighed either directly or after ignition. From the weight

of this body and its composition, the amount of the constituent in question is determined.

In *volumetric analysis,* instead of the final weighing of a definite body, a well-defined reaction is caused to take place, wherein the reagent is added in the form of a solution of which the strength (and hence the value for the reaction in question) is accurately known. The volume of this solution required to complete the reaction then becomes a measure of the substance acted upon. An example will make the distinction clear. The percentage of chlorine in a sample of sodium chloride may be determined by precipitation of the chlorine from a weighed portion as silver chloride, which is separated by filtration, ignited, and weighed (a *gravimetric* process); or the sodium chloride may be dissolved in water, and a solution of silver nitrate containing an accurately known amount of the silver salt in each cubic centimeter may be cautiously added until precipitation is complete, when the amount of chlorine may be calculated from the number of cubic centimeters of the silver nitrate solution involved in the reaction. This is a *volumetric* process, and is equivalent to weighing without the use of a balance.

Volumetric methods are generally more rapid, and frequently capable of greater accuracy, than gravimetric methods.

GENERAL DIRECTIONS FOR QUANTITATIVE WORK

The following paragraphs should be read carefully and thoughtfully. A prime essential for success as an analyst is attention to details and the avoidance of all conditions which could destroy or even lessen confidence in the analyses when completed, or in the accuracy of the results obtained. The suggestions here given are the outcome of much experience, and their adoption will tend permanently to insure work of a high grade, while neglect of them will often lead to disappointment and loss of time.

NEATNESS

The laboratory desk, and all apparatus, should be scrupulously neat and clean at all times. A sponge should always

be ready at hand, and desk and filter-stands should be kept dry and in good order. Funnels should never be allowed to drip upon the base of the stand. Glassware should always be wiped with a clean, lintless towel just before use.

WASH–BOTTLES

Wash-bottles, for distilled water, should be made from flasks of about 750 cc. capacity and be provided with gracefully bent tubes, which should not be too long. The jet should be connected with the tube entering the wash-bottle by a short piece of rubber tubing in such a way as to be flexible, and should deliver a stream about one millimeter in diameter. The neck of the flask may be wound with cord, or covered with wash leather, for greater comfort when hot water is used. It is well to provide several small wash-bottles for liquids other than distilled water, which should invariably be clearly labeled.

DESICCATORS

Desiccators should be filled with fused, anhydrous calcium chloride, over which is placed a clay triangle, or an iron triangle wound with platinum foil at those points which come into contact with a hot crucible. The cover of the desiccator should be made air-tight by the use of a thin coating of tallow.

Pumice moistened with sulphuric acid may be used in place of the calcium chloride, and is essential in special cases, but for most purposes the calcium chloride, if renewed occasionally and not allowed to cake together, is equally efficient.

Desiccators should never remain uncovered for any length of time. The dehydrating agents rapidly lose their efficiency on exposure to the air.

CRUCIBLES

Platinum crucibles should be employed for all ignitions and fusions, when possible. All crucibles, whether of platinum or porcelain, must be heated, and placed in a desiccator

to cool before use. This is to insure parallel conditions in separate weighings, which could not be obtained if the crucible were cooled in contact with the air, since a layer of moisture is then condensed on its surface, the amount varying with the humidity of the atmosphere. In the dry air of the desiccator this difficulty is avoided. The crucible should not be placed in the desiccator while very hot, but should be allowed to cool partially on the stand. If this precaution is observed, the air in the desiccator is less heated, and the ultimate cooling of the crucible to the temperature of the laboratory is hastened.

Crucibles should be cleaned, heated, and weighed before each analysis.

Platinum crucibles should be frequently scoured, either with sea sand or some preparation of the general character of "sapolio." Constant heating causes a slight crystallization of the surface of the platinum, which, if not removed, penetrates into the crucible. Gentle abrasion of the surface destroys the crystalline structure and prevents further damage. If sea sand is used great care is necessary to keep it from the desk, since beakers are easily scratched by it, and subsequently crack on heating.

Platinum crucibles stained by iron may often be cleaned by the use of potassium acid sulphate, or by heating with ammonium chloride. If the former is used, care should be taken not to heat so strongly as to expel all of the sulphuric acid, since the normal sulphate sometimes expands so rapidly on cooling as to burst the crucible.

Substances containing metals which might be reduced, with the formation of metallic buttons, must not be treated in platinum crucibles, as fusible alloys of platinum may be formed which ruin the crucible. Compounds of phosphorus or arsenic must not be heated under reducing conditions, since these elements, by contact with the platinum, render it brittle.

Liquids containing free chlorine, aqua regia, or ferric chloride all exert a solvent action upon platinum, the ferric chloride to a lesser degree than the others. Care must be

taken to prevent injury to platinum utensils, or the introduction of platinum into solutions by a disregard of these facts.

Caustic alkalies and peroxides of the alkalies attack platinum freely. Fusions with these fluxes should be made in silver, nickel, or iron crucibles, according to the special conditions of analysis.

EVAPORATION OF LIQUIDS

Too great care cannot be taken to prevent loss of solutions during processes of evaporation, either from too violent ebullition, from evaporation to dryness and spattering, or from the evolution of gas during the heating. In general, evaporation upon the steam bath is to be preferred to other methods on account of the impossibility of loss by spattering. If the steam baths are well protected from dust, solutions should be left without covers during evaporation; but solutions which are boiled upon the hot plate, or from which gases are escaping, should invariably be covered. In any case a watch-glass may be supported above the vessel by means of a glass triangle, or other similar device, and the danger of loss of material or contamination by dust thus be avoided.

It is obvious that evaporation is promoted by the use of vessels which admit of the exposure of a broad surface to the air.

Liquids which contain suspended matter (precipitates) should always be cautiously heated, since the presence of the solid matter is frequently the occasion of violent "bumping," with consequent risk to apparatus and analysis.

Liquids should never be transferred from one vessel to another, nor to a filter, without the aid of a stirring rod held firmly against the side or lip of the vessel. When the vessel is provided with a lip it is not usually necessary to use tallow or vaseline to prevent the loss of liquid by running down the side; whenever this seems imminent a *very thin* layer of tallow, applied with the finger to the edge of the vessel, will suffice. The stirring rod, down which the

liquid runs, should never be drawn upward in such a way as to allow the solution to collect on the under side of the rim of a beaker.

The number of transfers of liquids from one vessel to another during an analysis should be as small as possible to avoid the risk of slight losses. Each vessel must, of course, be completely washed to insure the transfer of all material; but it should be remembered that this can be accomplished better by the use of successive small portions of wash-water (perhaps 5–10 cc.), if each wash-water is allowed to drain away for a few seconds, than by the addition of large amounts which unnecessarily increase the volume of the solutions, causing loss of time in subsequent filtrations or evaporations.

REAGENTS

Whenever it is practicable, the amount of the reagent required should be calculated and a large excess avoided. Many analyses are spoiled by a neglect of this precaution.

Reagents should be carefully examined for impurities. If these are found, blank analyses must be made using only the reagents, and the amounts thus found deducted from the weights of contaminated precipitates. All reagents should, therefore, be measured, and a record of the amounts used should be made in the notebook.

The habit of carefully testing reagents, including distilled water, cannot be too early acquired or too constantly practiced; for, in spite of all reasonable precautionary measures, inferior chemicals will occasionally find their way into the stock room, or errors will be made in filling reagent bottles. The student should remember that while there are others who share the responsibility for the purity of materials in the laboratory of an institution, the responsibility will later be one which must be individually assumed.

The stoppers of reagent bottles should never be laid upon the desk, unless upon a clean watch-glass or paper. The neck and mouth of all such bottles should be kept scrupulously clean, and care taken that no confusion of stoppers occurs.

PRECIPITATION

From theoretical considerations it appears that no substance is to be regarded as absolutely insoluble in a specific medium, although the solubility of many which we term insoluble substances is less than can be measured by the means at our disposal. Successful precipitation must involve conditions which insure the nearest approximation to insolubility of the precipitated body, and the precipitate must also be in a form favorable for filtration and washing. For crystalline precipitates, the latter condition is fulfilled when the crystals are relatively large. This is often attained by allowing the fine crystals which first separate to digest in contact with the hot liquid from which they have fallen. During this digestion the smaller crystals, which are very slightly more soluble than the larger ones, redissolve, and since the solution is supersaturated as regards the larger crystals, the latter again precipitate. This transfer is further promoted by the influence of surface tension, which tends to reduce the surface of the solid, i. e., to increase the size of the individual crystals.

Certain amorphous bodies, such as ferric hydroxide, aluminium hydroxide, and silicic acid, may pass into a colloidal state, in which they form semi-solutions. This may happen if an attempt is made to precipitate them from solutions which are free from other salts. These rarely occur in analysis; but during the washing of these precipitates such semi-solutions may sometimes be formed, unless some salt is added to the wash-water. In cases where the addition of a salt to the wash-water is impracticable, the precipitate should be digested for some time on the steam bath in contact with the original solution, a procedure which lessens its tendency to pass into the colloidal state.

In all precipitations the reagent should be added slowly, with constant stirring, and should be hot when circumstances permit. The slow addition is less likely to occasion contamination of the precipitate by the inclosure of other substances which may be in the solution, or of the reagent itself.

For the complete removal of precipitates from containing vessels, it is often necessary to rub the sides of these vessels to loosen the adhering particles. This can best be done by slipping over the end of a stirring rod a piece of soft rubber tubing, which has been well washed to remove loose fragments, or by using a piece of sheet rubber, which may be folded over the rod and cemented together by moistening the surfaces with benzene. The sides of the beaker can then be rubbed with the covered rod.

All stirring rods should have the ends rounded in the flame to avoid scratching the beakers.

FILTRATION, AND THE TESTING OF FILTRATES AND WASHINGS

Distilled water should be employed in all quantitative work, and filtration should be made only through "washed filters," *i. e.*, those which have been treated with hydrochloric and hydrofluoric acids, and which, on incineration, leave a small and definitely known weight of ash. Such filters are readily obtainable in the market.

Funnels should be selected which have an angle as near 60° as possible, and with a narrow stem about six inches in length. The filter should be accurately folded to fit the funnel, and placed so that the top of the filter is about one-fourth inch below the top of the funnel. Under no circumstances should the filter extend above the edge of the funnel, as it is then utterly impossible to effect complete washing.

To test the efficiency of the filter, fill it with distilled water; this water should soon fill the neck completely, forming a continuous column of liquid which, by its hydrostatic pressure, produces a gentle suction, materially promoting the rapidity of filtration. Unless the filter allows a free passage of water under these conditions, its use is likely to prove a source of annoyance.

The use of a vacuum pump to promote filtration is rarely altogether advantageous in quantitative analysis, if paper filters are employed. The tendency of precipitates to pass

through the pores of the filter is increased, and this source of danger more than compensates for the possible gain in time. Exception may be made in the case of such precipitates as the hydroxides of chromium, aluminium, or iron, and of silicic acid; but whenever suction is applied, the point of the paper filter must be supported by a perforated platinum cone or a small "hardened filter" of parchment. The rate of filtration is often greater when an asbestos felt (Gooch filter) is used (see page 24 for a description), and the possibility of a substitution of this for the paper filter should always be considered.

When the filtrate is received in a beaker, the stem of the funnel should touch the side of the receiving vessel to avoid loss by spattering. Neglect of this precaution is a frequent source of error.

The vessels which contain the initial filtrate should *always* be replaced by clean ones, properly labeled, before the washing of a precipitate begins. In many instances a finely divided precipitate which shows no tendency to pass through the filter at first, while the solution is relatively dense, appears at once in the washings. Under such conditions the advantages accruing from the removal of the first filtrate are obvious, both as regards the diminished volume requiring refiltration, and also the lesser amount of washing subsequently required.

Much time may often be saved by washing precipitates by decantation, *i. e.*, by pouring over them, while still in the original vessel, considerable volumes of wash-water and allowing them to settle. The supernatant, clear wash-water is then decanted through the filter, so far as is practicable without disturbing the precipitate, and a new portion of wash-water is added. This procedure can be employed to special advantage with gelatinous precipitates, which fill up the pores of the filter paper. As the medium from which the precipitate is to settle becomes less dense it subsides less readily, and it becomes necessary to transfer it to the filter and complete the washing there.

A precipitate should never fill the filter completely, and the wash-water should be applied at the top of the filter, above the precipitate. It may be shown mathematically that the washing is most *rapidly* accomplished by filling the filter well to the top with wash-water each time, and allowing it to drain completely after each addition; but that when a precipitate is to be washed with the *least possible volume* of liquid the latter should be applied in repeated small quantities. For a discussion of this matter and the phenomena of adsorption, the student is referred to Ostwald's *Foundations of Analytical Chemistry,* page 15, *et seq.*

Gelatinous precipitates should not be allowed to dry before complete removal of foreign matter is effected. They are likely to shrink and crack, and subsequent additions of wash-water pass through these channels only.

Solutions should be filtered while hot, as far as possible, since the motion of the liquid through the pores of a filter is retarded by friction, and this for water at 100° C. is less than one-sixth of the resistance at 0° C.

All filtrates and wash-waters without exception must be properly tested. *This lies at the foundation of accurate work,* and the student should clearly understand that it is only by the invariable application of this rule that assurance of ultimate reliability can be secured. Every original filtrate must be tested to prove complete precipitation of the compound to be separated, and the wash-waters must also be examined. In testing the latter, the amount first taken should be but a few drops if the filtrate contains material which is to be subsequently determined. When, however, the washing of the filter and precipitate is nearly completed the amount should be increased, and for the final test not less than 3 cc. should be used.

It is impossible to trust to one's judgment with regard to the washing of precipitates; the washings from *each precipitate* of a series simultaneously treated must be tested, since the rate of washing will often differ materially under apparently similar conditions. *No exception can ever be made to this rule.*

The habit of placing a clean filter paper under the receiving beaker during filtration is one to be commended. On this paper a record of the number of washings can very well be made as the portions of wash-water are added.

It is an excellent practice, when possible, to retain filtrates and precipitates until the completion of an analysis, in order that, in case of question, they may be examined to discover sources of error.

IGNITION OF PRECIPITATES

The larger number of precipitates may, if proper precautions are taken, be ignited without previous drying. If, however, such precipitates can be dried without loss of time to the analyst (as, for example, over night), it is well to submit them to this process. It should, nevertheless, be remembered that a partially dried precipitate requires as much, or more care during ignition than a thoroughly moist one.

The precipitate, with the filter folded over it, should be placed well at the base of the crucible, which should then be placed so far above the lamp (using a small flame) that no violent escape of steam is possible. When the filter and contents have dried, the crucible should be placed on its side without the cover, and the heat should be gently increased until the filter chars, but should never be increased beyond this point until all volatile matter from the dry distillation of the filter paper has been expelled without taking fire. Much annoyance will be avoided by observing this point.

During this preliminary heating the flame should be placed near the mouth of the crucible, but in all subsequent heating the flame of the lamp should be well at the base of the crucible, as it is inclined upon its side, to allow a ready access of oxygen and to avoid the entrance of unburned (reducing) gases. When the filter has charred, the heat should be raised to redness until ignition is complete. The heating of precipitates over the blast lamp is to be avoided unless specially directed.

The limited number of instances in which the precipitate

must be separated from the filter preliminary to ignition will be treated of as they occur.

The analytical balance is a delicate instrument which will perform excellent service under careful treatment, but such treatment is an essential condition if its accuracy is to be depended upon. The following rules may be regarded as embodying the important points involved in the care of a balance; but no rules can do away with the necessity for a sense of personal responsibility on the part of each student, since by carelessness he can render inaccurate not only his own analyses, but those of all other students using the same balance:

1. The balance-pans should be brushed off and the adjustment of the balance tested before use, particularly where several persons use the same instrument.

To determine whether or not the balance is in adjustment, note (1) whether it is level; (2) whether the pointer rests at zero when the beam is lifted from its knife-edges, and also when lowered so that the pan arrests touch the scale pans; (3) that the mechanism for raising and lowering the beams works smoothly; (4) that the pan arrests touch the pans when the beam is lowered; and (5) that the needle swings equal distances on either side of the zero-point when set in motion without any load on the pans. If the latter condition is not fulfilled, the balance should be adjusted, unless the variation is not more than one division on the scale; it is often better to make a proper allowance for this small zero error than to disturb the balance by an attempt at correction.

Unless a student thoroughly understands the construction of a balance he should never attempt to make adjustments, but should apply to the instructor in charge. For a discussion of the construction and essential characteristics of a balance the student is referred to Fresenius' *Quantitative Analysis,* and to the admirable discussion of this topic in Morse's *Exercises in Quantitative Chemistry.*

2. The beam should never be set in motion by lowering it forcibly upon the knife-edges, nor by touching the pans, but rather by means of the rider (unless the balance be provided with some of the newer devices for the purpose), and the swing should be arrested only when the needle passes the zero on the scale, otherwise the knife-edges become dull. For the same reason the beam should never be left upon its knife-edges, nor should weights be removed from, or placed on the pans without supporting the beam, except in the case of the small fractional weights.

3. In testing the weight of a body, the weights should be applied in the order in which they occur in the weight-box (not at haphazard), and the weight should be recorded first by noting the weights missing from the weight-box, and that record subsequently checked as these weights are taken from the pan. This practice will often avoid or detect errors.

4. The balance-case should always be closed during the final weighing, when the rider is used, to protect the pans from the influence of air currents.

Before the final determination of an exact weight the beam should always be lifted from the knife-edges and again lowered into place, as it frequently happens that the scale pans are twisted by the impact of the weights, the beam being thereby virtually lengthened or shortened. Lifting the beam restores the proper alignment.

After the weighing is finished, the weights should always be replaced in their proper places in the weight-box and the rider taken from the beam.

The care of the weights is not less important than that of the balance, and these should always be standardized by the analyst, unless it is definitely known that they are in satisfactory condition. For a method of standardizing weights the student is referred to a paper by T. W. Richards, *J. Am. Chem. Soc.*, **22**, 144, or to Morse's *Exercises in Quantitative Chemistry*.

5. No chemical substance should ever be placed directly upon the balance-pan. Every substance or vessel weighed

should be *dry* and *cold*. A warm object occasions the formation of air currents, which vitiate the accuracy of the weight.

6. Above all, if any damage be done to a balance, if any substance be spilled upon the pans, or if the mechanism appear to be deranged, the matter should receive immediate attention, and should be reported at once to the instructor in charge. In the majority of instances serious damage can be averted by prompt action, when delay might ruin the balance.

<div style="text-align:center">NOTEBOOKS</div>

Notebooks should contain, beside the record of observations, descriptive notes. All records of weights should be placed upon the right-hand page, while that on the left is reserved for the notes, calculations of factors, or the amount of reagents required.

The neat and systematic arrangement of the records of analyses is of the first importance, and is an evidence of careful work and an excellent credential. Of two notebooks in which the results may be, in fact, of equal value as legal evidence, that one which is neatly arranged will carry with it greater weight.

All records should be dated, and all observations should be recorded at once in the notebook. The making of records upon loose paper is a practice to be deprecated, as is also that of copying original entries into a second notebook. The student should accustom himself to orderly entries at the time of observation.

The descriptive notes should mention any special difficulties encountered in the analyses and the remedies applied, and also incidents in the course of the analysis, if any, which may possibly influence the results injuriously. All analyses should be made in duplicate, and in general a close agreement in results should be expected. It should, however, be remembered that a close concordance of results in "check analyses" is not conclusive evidence of the accuracy of those results, although the probability that such is the case is, of

course, considerably enhanced. The satisfaction in obtaining "check results" in such analyses must never be allowed to interfere with the critical examination of the procedure employed, nor must they ever be regarded as in any measure a substitute for absolute truth and accuracy.

ECONOMY OF TIME

An economical use of laboratory hours is best secured by acquiring a thorough knowledge of the character of the work to be done before undertaking it, and then by so arranging the work that no time shall be wasted during the evaporation of liquids and like time-consuming operations. To this end the student should read thoughtfully not only the procedure, but the explanatory notes as well, before any step is taken in the analysis.

Several analyses should be in progress at once, and confusion carefully guarded against by a free use of labels.

In general, economy of time results from the filtration of several solutions at once, since the washing of five or more precipitates may frequently be accomplished in the time requisite for any one, if taken alone.

ACCURACY AND INTEGRITY DEMANDED

The fundamental conception of quantitative analysis implies a necessity for all possible care in guarding against loss of material or the introduction of foreign matter. All filters and solutions should be covered to protect them from dust, just as far as is practicable, and every particle of solution or precipitate must be regarded as invaluable for the success of the analysis.

In this connection it must also be emphasized that only the operator himself can know the whole history of an analysis, and only he can know whether his work is worthy of full confidence. No work should be continued for a moment after such confidence is lost, but should be resolutely discarded as soon as a cause for distrust is fully established. The student should, however, determine to put forth his best

efforts in *each* analysis; it is well not to be too ready to condone failures and to "begin again," as much time is lost in these fruitless attempts. *Nothing less than absolute integrity is or can be demanded of a quantitative analyst, and any disregard of this principle, however slight, is as fatal to success as lack of chemical knowledge or inaptitude at manipulation can possibly be.*

PART II

GRAVIMETRIC ANALYSIS

DETERMINATION OF CHLORINE IN SODIUM CHLORIDE

PREPARATION

THE preparation of chemically pure sodium chloride from the commercial article may be effected as follows:

Procedure.—Weigh out, upon rough balances, about 50 grams of a sample of "table salt"; cover this with 120 cc. of distilled water, stir until the water is saturated, and filter. To the filtrate add concentrated hydrochloric acid (sp. gr. 1.20) until the chloride begins to separate, then pass into the solution gaseous hydrogen chloride. This should be generated in a flask, from rock salt and commercial sulphuric acid. The gas should be washed by passing it through concentrated, aqueous hydrochloric acid, and the delivery-tube should terminate in a 2-inch funnel, placed mouth downward, to prevent the clogging of the delivery-tube by the separated salt. When the separation of the salt has apparently ceased, remove it by filtration upon a paper disc placed upon a perforated porcelain plate (a Witt filter), and drain by suction. Wash the chloride with 25 cc. of hydrochloric acid (sp. gr. 1.12) in successive small portions, allowing the precipitate to drain completely after each addition. Wash finally with a small quantity (5 cc.) of water, and test this wash-water for sulphates. If sulphates are found, the washing with hydrochloric acid must be continued. When freed from sulphates, transfer the precipitate to a porcelain or platinum dish or crucible, and heat until decrepitation ceases. The chloride* should then be allowed to cool in a desiccator, and be placed in a weighing-tube, or weighing-bottle, which should be kept tightly stoppered.

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Notes.—1. The commercial grades of table salt contain as impurities chlorides or sulphates of magnesium, calcium or potassium, the two first-named chlorides causing the salt to absorb moisture. When hydrochloric acid is added to a saturated solution of the salt, sodium chloride is thrown down, leaving the impurities in solution. The principles underlying the separation are the following: The solution is saturated with reference to sodium chloride. According to the law of mass action (see Appendix), the condition of equilibrium within such a solution may, in general, be expressed thus:

$$\frac{Conc'n\ Na^+\ ions \times Conc'n\ Cl^-\ ions}{Conc'n\ NaCl} = Const.$$

When the readily soluble hydrogen chloride gas is passed into this solution, the concentration of the Cl^--ions in the solution is much increased, and it is plain that if the value of the constant in the above expression is to remain unchanged, as it should if the law is valid, the concentration of the Na^+-ions must diminish, which means that the concentration of the undissociated NaCl must increase. But the solution is, as stated, already saturated with reference to sodium chloride, and the newly formed NaCl must, therefore, separate from the solution.

This explanation is not, however, sufficient to account for the large proportion of the sodium chloride which it is possible to separate by means of the hydrogen chloride gas. It appears to be further true that the undissociated sodium chloride is much less soluble in the concentrated hydrochloric acid which is formed than it is in water. This, in turn, seems to be due to the association of the water molecules with those of the acid (or its ions) to form hydrated compounds, as a consequence of which the solvent power of the water for sodium chloride is greatly lessened. The solubility of those substances which are present in the salt as impurities is not similarly affected, and purification from them is therefore a possibility. This is not an economical procedure for the production of pure sodium chloride on a commercial scale.

2. The precipitation of the sodium chloride might be effected more quickly by the addition of liberal quantities of

concentrated aqueous hydrochloric acid, but its purity is less certain under those conditions. The slow separation caused by the absorption of the gas is more favorable to the formation of a pure product, and the process is also somewhat more economical if carried out in this way.

3. Since the sodium chloride is not insoluble in either the acid or the water used for washing, it is essential that these should be used in as small quantities as is practicable. Note the statement on page 10 concerning the most efficient method of washing a precipitate with a limited quantity of liquid.

4. The heating of the chloride is essential to expel any excess of hydrochloric acid held by the salt, and to remove moisture inclosed between crystal surfaces. The escape of this moisture is the cause of decrepitation. Even the pure salt is slightly hygroscopic; hence the necessity for cooling in the dry air of the desiccator and for preservation in stoppered tubes.

<center>ANALYSIS</center>

The sodium chloride, prepared as above, is ready for analysis, and if the preparation has been carefully made the percentage of chlorine found on analysis should agree closely with that calculated from the formula NaCl.

Procedure.—(*a*) Carefully clean the weighing-tube containing the sodium chloride, handling it as little as possible with the moist fingers, and weigh it accurately to 0.0001 gram, recording the weight at once in the notebook. Hold the tube over the top of a 300 cc. lipped beaker, and cautiously remove the stopper, noting carefully that no particles fall from it, or from the tube, elsewhere than into the beaker. Pour out a small portion of the chloride, replace the stopper, and determine by approximate weighing how much has been removed. Continue this procedure until 0.25–0.30 gram has been taken from the tube, then weigh accurately and record the weight beneath the first in the notebook. The difference of the two weights represents the weight of the chloride taken for analysis. Again weigh a second portion of 0.25–0.30 gram into a second beaker of the same size as

the first. The beakers should be plainly marked to correspond with the entries in the notebook. Dissolve each portion of the chloride in. 150 cc. of distilled water, and add about ten drops of nitric acid (sp. gr. 1.20). Calculate the volume of silver nitrate solution required to effect complete precipitation in each case, and add slowly about 5 cc. in excess of that amount, with constant stirring. Heat the solutions cautiously to boiling, stirring occasionally, and continue the heating and stirring until the precipitates settle promptly, leaving a nearly clear supernatant liquid. This heating should not take place in direct sunlight. The beaker should be covered with a watch-glass, and both boiling and stirring so regulated as to preclude any possibility of loss of material. Add to the clear liquid one or two drops of silver nitrate solution, to make sure that an excess of the reagent is present. Prepare two washed filters (9 cm. in diameter), bearing in mind the precautions mentioned on pages 8 and 9, and pour the liquid through the filter, leaving the chloride in the beaker as far as possible. Examine the filtrates carefully to make certain that they are perfectly free from particles of silver chloride, and add two or three drops of silver nitrate solution to each, to test for complete precipitation. If no precipitate appears in the course of five minutes, remove these filtrates, and replace them by clean beakers. (The filtrates should then be poured into the laboratory receptacle for "silver residues.") Wash the precipitates two or three times by decantation with hot water, transfer them to the filter by means of a stream from the wash-bottle, with the aid of a stirring rod with a rubber tip. Now wash the filters and precipitates until 3 cc. of the washings show no cloudiness with a *drop* of hydrochloric acid. The funnels should then be covered with a filter paper which has been previously moistened and stretched over the sides of the funnel, to which it will adhere on drying. It should be properly labeled with the student's name and desk number, and then placed in a drying closet, at a temperature of about 100–110° C., until completely dry.

The perfectly dry filter is then opened over a circular piece of clean, smooth, glazed paper about six inches in diameter, placed upon a larger piece about twelve inches in diameter. The precipitate is removed from the filter as completely as possible by rubbing the sides gently together, or by scraping them cautiously with a feather which has been cut close to the quill and is slightly stiff. In either case, care must be taken not to rub off any considerable quantity of the paper, nor to lose silver chloride in the form of dust. Cover the precipitate on the glazed paper with a watch-glass to prevent loss of fine particles and to protect it from dust. Fold the filter paper carefully, as it was when it came from the funnel, roll it into a small cone, and wind loosely around *the top* a piece of small platinum wire. Hold the filter by the wire over a No. 7 porcelain crucible (which has been cleaned, ignited, cooled in a desiccator, and weighed), ignite it, and allow the ash to fall into the crucible. Place the crucible upon a clean clay triangle, on its side, and ignite, with the flame well at its base, until all the carbon of the filter has been consumed. Allow the crucible to cool, add two drops of nitric acid and one drop of hydrochloric acid, and heat *very cautiously,* to avoid spattering, until the acids have been expelled; then transfer the main portion of the precipitate from the glazed paper to the cooled crucible, placing the latter for the purpose on the larger piece of glazed paper and brushing the precipitate from the smaller piece into it, sweeping off all particles belonging to the determination.

Moisten the precipitate with two drops of nitric acid and one drop of hydrochloric acid, and again heat with great caution until the acids are expelled and the precipitate is white, when the temperature is *gradually* raised until the silver chloride begins to fuse. The crucible is then cooled in a desiccator and weighed, after which the heating (without the addition of acids) is repeated, and it is again weighed. This must be continued until the weight is constant within 0.0003 gram in two consecutive weighings. Deduct the

weight of the crucible, and calculate the weight of chlorine in the silver chloride, and subsequently the percentage in the sample of sodium chloride taken for analysis. Consult Paragraph 1, Part IV.

Notes.—1. The nitric acid is added before precipitation to lessen the tendency of the silver chloride to carry down with it other substances which might be precipitated from a neutral solution. A large excess of the acid would exert a slight solvent action upon the chloride.

2. The solution should not be boiled after the addition of the nitric acid before the presence of an excess of silver nitrate is assured, since a slight interaction between the nitric acid and the sodium chloride is possible, by which a loss of chlorine, either as such or as hydrochloric acid, might ensue. The presence of an excess of the precipitant can usually be recognized at the time of its addition, by the increased readiness with which the precipitate clots together and settles.

3. The precipitate should not be exposed to strong sunlight, since by its action a reduction of the silver chloride is effected, accompanied by a loss of chlorine. The superficial alteration which the chloride undergoes in diffused daylight is not fatal to the accuracy of the determination, since the slight loss of chlorine may be counteracted by the treatment of the precipitate with nitrohydrochloric acid, as noted below.

4. The precipitate must be washed with hot water until it is absolutely free from silver and sodium nitrates. It may be assumed that the sodium is also completely removed when the wash-water shows no evidence of silver. It must be borne in mind that silver chloride is somewhat soluble in hydrochloric acid, and only a single drop should be added. The washing should be continued until no cloudiness whatever can be detected in 3 cc. of the washings.

5. The separation of the silver chloride from the filter is essential, since the burning carbon of the paper would reduce a considerable quantity of the precipitate to metallic silver, and its complete reconversion to the chloride within the crucible, by means of acids, would be accompanied by some uncertainty. The small amount of precipitate which adheres

to the filter is, it is true, partially reduced to metallic silver during the ignition; but this small quantity can be dissolved in the nitric acid which is added, and completely reconverted to chloride by the hydrochloric acid. The subsequent addition of these two acids to the main portion of the precipitate restores the chlorine to any chloride which may have been reduced by the sunlight.

The platinum wire is wrapped around the top of the filter during its incineration to avoid contact with any reduced silver from the reduction of the precipitate. If the wire was placed nearer the apex, such contact could hardly be avoided.

6. Silver chloride should not be heated to complete fusion, since a slight loss by volatilization is possible at high temperatures. The temperature of fusion is not always sufficient to destroy filter shreds; hence these should not be allowed to contaminate the precipitate.

7. The ignited precipitate of silver chloride, as well as the filtrates which contain an excess of silver nitrate, should be placed in the jar for "silver residues," as the silver can be easily recovered and converted into silver nitrate crystals for laboratory use. The crucible may be cleaned by placing in it some granulated zinc and dilute sulphuric acid. The chloride is soon loosened, and may be detached.

8. Cork stoppers in weighing-tubes are likely to change in weight from the varying amounts of moisture absorbed from the atmosphere. It is, therefore, necessary to confirm the recorded weight of a tube which has been unused for some time before weighing out a new portion of substance from it.

9. Silver chloride is but slightly soluble in water. The solubility varies with its physical condition within small limits, and is about 0.0018 gram per liter at 18° C. for the curdy variety usually precipitated. It is readily soluble in ammonium hydroxide with the formation of a complex ion, $Ag(NH_3)_2^+$, from the NH_3 molecules present to some extent in the hydroxide solution. It is also soluble in alkali cyanide solutions with the formation of a complex anion, $Ag(CN)_2^-$, and in alkali thiosulphate solution, apparently as an anion of the formula, $AgS_2O_3^-$. The chloride is also somewhat soluble in an excess of hydrochloric acid, possibly with the

formation of $AgCl_2^-$ anions, and also slightly soluble in solutions of many chlorides, of silver nitrate, and in nitric acid if concentrated.

10. If the student has occasion to search for numerical data regarding solubilities of precipitates, or more extended statements regarding properties of precipitates, or to seek for a greater variety of methods of determination than can be appropriately included in this manual, he should consult such reference books as Roscoe and Schorlemmer's *Treatise on Chemistry,* Fresenius' *Quantitative Analysis,* Treadwell-Hall's *Analytical Chemistry,* Vol. II, Comey's *Dictionary of Solubilities,* or some of the general dictionaries of chemistry; and may also, under advice from an instructor, consult chemical journals for the results of the most recent investigations. This statement is equally applicable to all subsequent procedures.

DETERMINATION OF CHLORINE IN SODIUM CHLORIDE, WITH THE USE OF A GOOCH FILTER

A commercial sample of table salt may advantageously be substituted for the pure sodium chloride, if the latter has already been examined. The table salt should be heated until decrepitation ceases, and cooled in a desiccator.

Procedure.—(*b*) Weigh out two portions of the substance, each weighing about 0.25 gram, and precipitate the silver chloride as described in procedure (*a*). Meanwhile prepare a Gooch filter as follows: Select a small glass funnel, 1 to 1¼ inches in diameter (or a funnel tube, as described in Note 2), and stretch over its mouth a piece of rubber-band tubing ("bill-tie tubing") about 1 inch wide and 1½ inches long. This should be drawn down on the sides of the funnel until it holds firmly, leaving an opening at the center of the mouth of the funnel, into which a perforated porcelain crucible (Gooch crucible) is fitted. The rubber should be drawn up around the sides of the crucible until it is air-tight. Fit the glass funnel into the stopper of a filter bottle, and connect it with the vacuum pump. Suspend some finely divided asbestos, which has been washed with acid, in 20 to 30 cc.

of water; allow this to settle, pour off the very fine particles, and then pour some of the mixture cautiously into the crucible until an even felt of asbestos, not over $\frac{1}{32}$ inch in thickness, is formed. A gentle suction must be applied while preparing this felt. Wash the felt thoroughly by passing through it distilled water until all fine or loose particles are removed, increasing the suction at the last until no more water can be drawn out of it; place on top of the felt the small, perforated porcelain disc; then place the crucible in a small beaker, and place both in a drying closet at 120–130° C. for thirty to forty minutes. Cool the crucible in a desiccator, and weigh. Heat again for twenty to thirty minutes, cool, and again weigh, repeating this until the weight is constant within 0.0003 gram. The filter is then ready for use.

Replace the crucible in the funnel, and apply a gentle suction, *after which* the solution to be filtered may be poured in without disturbing the asbestos felt. When pouring liquid into a Gooch filter, hold the stirring rod well down in the crucible, so that the liquid does not fall with any force upon the asbestos.

Examine the first portions of the filtrate which pass through the filter with great care for asbestos fibers, which are most likely to be lost at this point. Refilter the liquid if any fibers are visible. Transfer the whole of the precipitate to the filter, and wash thoroughly with hot water until free from soluble silver salts, then dry at 120–130° C. to a constant weight. The percentage of chlorine may be calculated from the weight of silver chloride.

Notes.—1. The asbestos should be of the finest quality and capable of division into minute fibrous particles. A coarse felt is not satisfactory.

The use of the Gooch filter commends itself strongly when a considerable number of halogen determinations are to be made, since successive portions of the silver halides may be filtered on the same filter, without the removal of the preceding portions, until the crucible is about two-thirds filled. If the felt is properly prepared, filtration and washing are

rapidly accomplished on this filter, and this, combined with
the possibility of collecting several precipitates on the same
filter, is a strong argument in favor of its use with any but
gelatinous precipitates. If perforated platinum crucibles are
employed, which can be fitted into a platinum cap after re-
moval from the funnel, the precipitates can be ignited over
the flame of a lamp as in an ordinary platinum crucible. The
asbestos is apt to curl away from the edges during
such heating, and if the same filter is used for a
second time great care is required to prevent loss
of asbestos. The filtrate should always be carefully
examined for asbestos fibers, and refiltered if any
are found.

2. A funnel tube made from stout glass tubing
about 1¼-inch inside diameter and 3 inches long,
which is closed at one end except for an attached
stem, like that of an ordinary funnel, of suitable
size and length to pass through a rubber stopper,
may be substituted for the ordinary glass funnel
above prescribed (Fig. 1). It is then only necessary
to cover the upper edges of this tube with rubber. The
crucible, being only a little larger in diameter, may be pressed
into it, making an air-tight connection.

Fig. 1

DETERMINATION OF IRON AND OF SULPHUR IN FERROUS AMMONIUM SULPHATE
$FeSO_4.(NH_4)_2SO_4.6H_2O$
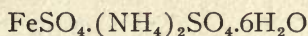
DETERMINATION OF IRON

Procedure.—Select a quantity of perfectly clear crystals of the salt sufficient to fill a weighing-tube. Weigh out into two 200 cc. lipped beakers two portions of about 1 gram each, and dissolve these in 50 cc. of water to which 1 cc. of hydrochloric acid (sp. gr. 1.12) has been added. Heat the solution to boiling, and while at the boiling point add nitric acid (sp. gr. 1.42), *drop by drop* (noting the volume used), until the brown coloration, which appears after the addition of a part of the nitric acid, gives place to a yellow or red. Avoid a large excess of nitric acid, but be sure that the action is complete. Pour this solution cautiously into about 200 cc. of water, containing a slight excess of ammonia. Calculate for this purpose the amount of aqueous ammonia required to neutralize the acids added, and also to precipitate the iron as ferric hydroxide from the weight of the ferrous ammonium sulphate taken for analysis. The volume thus calculated will be in excess of that actually required, since the acids are in part consumed in the oxidation process, or are volatilized. Heat the solution to boiling, and allow the precipitated ferric hydroxide to settle. Decant the clear liquid through a washed filter (9 cm.), keeping as much of the precipitate in the beaker as possible. Wash once by decantation with 100 cc. of hot water, and then transfer the bulk of the precipitate to the filter. Dissolve the iron from the filter with hot hydrochloric acid (sp. gr. 1.12), adding it in small portions and using as little as possible, and collect the solution in the beaker in which precipitation took place. Add 1 cc. of nitric acid (sp. gr. 1.42), boil for a few moments, and again pour into an excess of ammonia. Wash the precipitate twice by decantation, and finally transfer it to the filter; wash continuously with hot water until finally 3 cc.

of the washings, acidified with nitric acid, show no evidences of the presence of chlorides when tested with silver nitrate. (Note the precaution mentioned on page 10.) The filtrate and washings are combined with those from the first precipitation.

The precipitate, which may be moist, is placed in a platinum crucible which has been previously heated, cooled in a desiccator, and weighed. It is then treated according to the directions for "Ignition of Precipitates," page 11. When the volatile matter of the filter has been expelled, raise the temperature to the full heat of the burner for fifteen minutes. During this time the crucible should be inclined, the cover removed, and the flame well at the base of the crucible. Finally, heat over the blast lamp for three minutes with the crucible covered. Cool and weigh. Repeat the strong heating until the weight is constant within 0.0003 gram. Exercise great care when heating over the blast lamp that a small flame is used, and that this is directed against the bottom of the crucible in such a way as to preclude the entrance of unburned or reducing gases into it by reflection from the edges of the cover. From the weight of ferric oxide (Fe_2O_3) calculate the weight of iron (Fe) and the percentage of the latter in the sample.

Notes.—1. If a selection of *pure* material for analysis is to be made, those crystals which are cloudy are to be avoided on account of loss of water of crystallization; and also those which are red, indicating the presence of ferric iron. If, on the other hand, the value of an *average sample* of the material is desired, it is preferable to grind the whole together, mix thoroughly, and take a sample from the mixture for analysis.

2. The Fe^{++}-ions are readily oxidized by the oxygen of the air to Fe^{+++}-ions, with the simultaneous production of OH^--ions in the solution. In the neutral solution these tend to form a basic ferric sulphate which partially precipitates, and the addition of the hydrochloric acid, by the combination of its H^+-ions with the OH^--ions, prevents the formation of this basic compound.

It should be noted that if the Fe^{++}-ions are changed to Fe^{+++}-ions in a neutral solution, there are no longer sufficient aggregate negative charges on the SO_4^{--}-ions to balance the positive charges on the Fe^{+++}-ions. The OH^--ions formed as stated above supply this deficiency in the absence of any acid, while in the presence of the hydrochloric acid the Cl^--ions meet the requirement that the charges of opposite character shall be balanced within the solution.

3. The nitric acid, after attaining a moderate strength, oxidizes the Fe^{++}-ions to Fe^{+++}-ions with the formation of an intermediate nitrosocompound similar in character to that formed in the "ring-test" for nitrates. The nitric oxide is driven out by heat, and the solution then shows by its color the presence of ferric chloride. A drop of the oxidized solution should be tested on a watch-glass with potassium ferricyanide, to insure the absence of Fe^{++}-ions. This oxidation of the iron is necessary, since Fe^{++}-ions are not completely precipitated by ammonia.

The ionic changes which are involved in this oxidation are perhaps most simply expressed by the equation,

$$3Fe^{++} + NO_3^- + 4H^+ = 3Fe^{+++} + 2H_2O + NO,$$
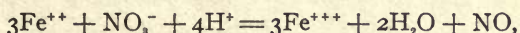
the H^+-ions coming from the acid in the solution, in this case either the nitric or the hydrochloric acid. The full equation on which this is based may be written thus: $6FeSO_4 + 2HNO_3 + 6HCl = 2Fe_2(SO_4)_3 + 2FeCl_3 + 2NO + 4H_2O$, assuming that only enough nitric acid is added to complete the oxidation.

4. The ferric hydroxide precipitate tends to carry down some sulphuric acid in the form of basic ferric sulphate. This tendency is lessened if the solution of the iron is added to an excess of OH^--ions from the ammonium hydroxide, since under these conditions immediate and complete precipitation of the ferric hydroxide ensues. On the other hand, a gradual neutralization with ammonia may result in the local formation of a neutral solution within the liquid, and subsequent deposition of a basic sulphate as a consequence of a deficiency of OH^--ions from the NH_4OH and a partial hydrolysis of the ferric salt. (See Appendix.) Even with this precaution the entire absence of sulphates from the first iron pre-

cipitate is not assured. It is, therefore, redissolved and again thrown down by ammonia. The organic matter of the filter paper may occasion a partial reduction of the iron during solution, with consequent possibility of incomplete precipitation with ammonia. The nitric acid is added to reoxidize this iron.

5. On the ignition of ferric oxide in the presence of ammonium chloride, volatile ferric chloride is formed with consequent loss of iron. The precipitate must, therefore, be completely washed. The washings are acidified with nitric acid, before testing with silver nitrate, to destroy the ammonia which is a solvent of silver chloride.

The use of suction to promote filtration and washing is permissible, though not prescribed. The precipitate should not be allowed to dry during the washing, for reasons stated on page 10.

6. To avoid errors arising from the solvent action of ammoniacal liquids upon glass, the iron precipitate should be filtered without unnecessary delay.

7. The directions for the ignition of precipitates (on page 11) must be closely followed. A ready access of atmospheric oxygen is of special importance to insure the reoxidation to ferric oxide of any iron which may be reduced to magnetic oxide (Fe_3O_4) during the combustion of the filter. The final heating over the blast lamp is essential for the complete expulsion of the last traces of water from the hydroxide.

8. Ignited ferric oxide is somewhat hygroscopic. On this account the weighings must be promptly completed after removal from the desiccator. In all weighings after the first it is well to place the weights upon the balance-pan before removing the crucible from the desiccator. It is then only necessary to move the rider to obtain the weight.

9. The gravimetric determination of aluminium or chromium is comparable with that of iron just described, with the additional precaution that the solution must be boiled until it contains but a very slight excess of ammonia, since the hydroxides of aluminium and chromium are more soluble than ferric hydroxide.

The most important properties of these hydroxides, other than those mentioned, are, from a quantitative standpoint,

the following. All are precipitated by the hydroxides of sodium and potassium, but always inclose some of the precipitant, and should be reprecipitated with ammonium hydroxide before ignition to oxides. Chromium and aluminium hydroxides dissolve in an excess of the caustic alkalies and form anions, probably of the formula AlO_2^- and CrO_2^-. Chromium hydroxide is reprecipitated from this solution on boiling. When first precipitated the hydroxides are all readily soluble in acids, but aluminium hydroxide dissolves with considerable difficulty after standing or boiling for some time. Their precipitation is promoted by the presence of ammonium chloride, but is partially or entirely prevented by the presence of tartaric or citric acids, glycerine, sugars, and some other forms of soluble organic matter. They each yield on ignition an oxide suitable for weighing (Al_2O_3, Cr_2O_3, Fe_2O_3).

DETERMINATION OF SULPHUR

Procedure.—Add to the combined filtrates from the ferric hydroxide about 0.6 gram of anhydrous sodium carbonate; cover the beaker, and then add hydrochloric acid in moderate excess and evaporate to dryness on the water bath. Add 10 cc. of hydrochloric acid (sp. gr. 1.12) to the residue, and again evaporate to dryness on the bath. Dissolve the residue in water, filter if not clear, transfer to a 700 cc. lipped beaker, dilute to about 400 cc., and cautiously add hydrochloric acid until the solution shows a distinctly acid reaction. Heat the solution to boiling, and add *very slowly*, and with constant stirring, 20 cc. in excess of the calculated amount of hot barium chloride solution (which should contain about 20 grams $BaCl_2.2H_2O$ per liter). Continue the boiling for about two minutes, allow the precipitate to settle, and decant the liquid at the end of half an hour. Replace the beaker containing the original filtrate by a clean beaker, wash the precipitated sulphate by decantation with hot water, and subsequently upon the filter until it is freed from chlorides. The filter is then transferred to a platinum crucible and ignited, as described on page 11, until the weight is constant.

To test the purity of the precipitates, mix each in the crucible with five to six times its weight of sodium carbonate. This can best be done by placing the crucible on a piece of glazed paper and stirring the mixture with a clean, dry stirring rod, which may finally be wiped off with a small fragment of filter paper, the latter being placed in the crucible. Cover the crucible and heat until a quiet liquid fusion ensues. As the fused mass cools, insert in it a piece of platinum wire, coiled so that it will hold securely in the solidified mass. When solidification is complete, replace the lamp under the crucible and heat only long enough to cause the outside of the mass to fuse. Now allow the crucible to cool completely, when the mass may usually be at once drawn out of the crucible by the wire. If it still adheres, a cubic centimeter or so of water may be placed in the cold crucible and cautiously brought to boiling, when the cake will become loosened and may be removed on the wire and suspended in about 250 cc. of hot distilled water to dissolve. Clean the crucible completely, rubbing the sides with a rubber-covered stirring rod, if need be.

When the fused mass has completely disintegrated and nothing further will dissolve, decant the solution from the residue of barium carbonate, pour over this residue 20 cc. of a solution of sodium carbonate and 10 cc. of water, and heat to gentle boiling for about three minutes. Filter off the carbonate and wash it with hot water, testing the slightly acidified washings for sulphate and preserving any precipitates which appear in these tests. Acidify the filtrate with hydrochloric acid until just acid, bring to boiling, and add hot barium chloride solution slowly, as before. Add also any tests from the washings in which precipitates have appeared. Filter, wash, ignite, and weigh. Compare the results with those first obtained, and calculate the weight of sulphur in the barium sulphate and from that the percentage in the ferrous ammonium sulphate.

Notes.—1. The ionic changes involved in the precipitation of barium sulphate are very simple: $Ba^{++} + SO_4^{--} = BaSO_4$.

This case affords one of the best illustrations of the effect of an excess of a precipitant in decreasing the solubility of a precipitate. If the conditions are considered which exist at the moment when just enough of the Ba^{++}-ions have been added to correspond to the SO_4^{--}-ions in the solution, it will be seen that nearly all of the barium sulphate has been precipitated, and that the small amount which then remains in the solution which is in contact with the precipitate must represent a saturated solution for the existing temperature, and that this solution is comparable with a solution of sugar to which more sugar has been added than will dissolve. It should be borne in mind that the quantity of barium sulphate in this *saturated solution* is a *constant quantity* for the existing conditions. The dissolved barium sulphate, like any electrolyte, is dissociated, and the equilibrium conditions may be expressed thus:

$$\frac{Conc'n\ Ba^{++} \times Conc'n\ SO_4^{--}}{Conc'n\ BaSO_4} = Const.,$$

or, since *Conc'n BaSO₄* for the saturated solution has a constant value (which is very small), it may be eliminated, when the expression becomes $Conc'n\ Ba^{++} \times Conc'n\ SO_4^{--} = Const.$, which is the "solubility product" of $BaSO_4$. If, now, an excess of the precipitant, a soluble barium salt, is added in the form of a relatively concentrated solution (the slight change of volume of a few cubic centimeters may be disregarded for the present discussion) the concentration of the Ba^{++}-ions is much increased, and as a consequence the $Conc'n\ SO_4^{--}$ must decrease in proportion if the value of the expression is to remain constant, which is a requisite condition if the law of mass action upon which our argument depends holds true. In other words, SO_4^{--}-ions must combine with some of the added Ba^{++}-ions to form $BaSO_4$; but it will be recalled that the solution is already saturated with $BaSO_4$, and this freshly formed quantity must, therefore, separate and add itself to the precipitate. This is exactly what is desired in order to insure more complete precipitation and greater accuracy, and leads to the conclusion that the larger the excess of the precipitant added the more suc-

cessful the analysis; but a practical limit is placed upon the quantity of the precipitant which may be properly added by other conditions, as stated in the following note.

2. Barium sulphate, in a larger measure than most substances, tends to carry down other substances which are present in the solution from which it separates, even when these other substances are relatively soluble, including the barium chloride used as the precipitant. This is also notably true in the case of nitrates and chlorates of the alkalies, and of ferric compounds; and, since in this analysis ammonium nitrate has resulted from the neutralization of the excess of the nitric acid added to oxidize the iron, it is essential that this should be destroyed by repeated evaporation with a relatively large quantity of hydrochloric acid. During evaporation a mutual decomposition of the two acids takes place, and the nitric acid is finally decomposed and expelled by the excess of hydrochloric acid.

Iron is usually found in the precipitate of barium sulphate when thrown down from hot solutions in the presence of ferric salts. This, according to Küster and Thiel (*Ztschr. anorg. Chem.*, **22**, 424), is due to the formation of a complex ion $[Fe(SO_4)_2]$ which precipitates with the Ba^{++}-ion, while Richards (*Ztschr. anorg. Chem.*, **23**, 383) ascribes it to hydrolytic action, which causes the formation of a basic ferric complex which is occluded in the barium precipitate. Whatever the character of the compound may be, it has been shown that it loses sulphuric acid upon ignition, causing low results, even though the precipitate contains iron. It is obvious that this error cannot be corrected by the process of purification described on page 32.

The contamination of the barium sulphate by iron is much less in the presence of ferrous than ferric salts. If, therefore, the sulphur alone were to be determined in the ferrous ammonium sulphate the precipitation by barium might be made directly from an aqueous solution of the salt, which had been made slightly acid with hydrochloric acid.

3. Barium sulphate is slightly soluble in hydrochloric acid, even dilute, probably as a result of the reduction in the degree of dissociation of sulphuric acid in the presence of the H^+-ions of the hydrochloric acid, and possibly, also,

owing to the formation of a complex anion made up of barium and chlorine; hence only the smallest excess should be added over the amount required to acidify the solution.

4. The precipitation of the barium sulphate is probably complete at the end of a half hour, and the solution may safely be filtered at the expiration of that time if it is desired to hasten the analysis.

As noted on page 7, many precipitates of the general character of this sulphate tend to grow more coarsely granular if digested for some time with the liquid from which they have separated. It is therefore well to allow the precipitate to stand in a warm place for several hours, whenever practicable, to promote ease of filtration. The filtrate and washings should, however, always be carefully examined for minute quantities of the sulphate which may pass through the pores of the filter. This is best accomplished by imparting to the liquid a gentle rotary motion, when the sulphate, if present, will collect in the center of the beaker. *All filtrates in this and other determinations must be tested for complete precipitation by adding to them a small quantity of the reagent and allowing them to stand.*

5. A reduction of barium sulphate to the sulphide may very readily be caused by the reducing action of the burning carbon of the filter, and much care should be taken to prevent any considerable reduction from this cause. Subsequent ignition, with ready access of air, reconverts the sulphide to sulphate unless a considerable reduction has occurred. In the latter case it is expedient to add one or two drops of sulphuric acid and to heat cautiously until the excess of acid is expelled.

6. Most impurities which are inclosed by the sulphate cannot be removed by washing with water; treatment with hydrochloric acid, even if it accomplishes the removal of these impurities, dissolves some of the sulphate, which must be recovered. It is advisable, then, in any case, and essential when the contamination is due to alumina or silica, to purify by fusion with sodium carbonate, as described in the procedure. By this process the impurities are either rendered insoluble and are removed by filtration with the barium carbonate, or, if they pass into solution with the sodium sulphate,

are present in such small amounts relatively that they fail to be carried down by a second precipitation of the sulphate. It is obvious that the excess of alkaline carbonate must be destroyed by hydrochloric acid, and that the same care must be taken in the addition of the barium chloride the second time as was taken at first. The reaction during fusion is the following:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$

7. The barium carbonate is boiled with sodium carbonate solution before filtration because the equation above is reversible; and it is only by keeping the sodium carbonate present in excess until nearly all of the sodium sulphate solution has been removed by filtration that the reversion of some of the barium carbonate to barium sulphate is prevented. This is an application of the principle of mass action, in which the concentration of the reagent (the carbonate ion) is kept as high as practicable and that of the sulphate ion as low as possible, in order to force the reaction in the desired direction. (See Appendix.)

8. The removal of the fused mass from the crucible is facilitated by the procedure outlined, because the crucible springs away from the mass inside after the second brief heating, since it cools and contracts more rapidly. The boiling with water is sometimes necessary to dissolve a slight ring of carbonate which solders the mass to the crucible at its upper edge.

9. Barium sulphate requires about 400,000 parts of water for its solution. It is not decomposed at a red heat, but suffers loss, probably of sulphur trioxide, at a temperature above 900° C.

DETERMINATION OF PHOSPHORIC ANHYDRIDE IN APATITE

The sample of apatite selected for analysis should be as nearly pure as possible. Specimens of the mineral which leave but a slight siliceous residue are not difficult to secure.

Procedure.—Grind the mineral in an agate mortar until no grit is perceptible. Transfer the substance to a weighing-tube, and weigh out two portions, not exceeding 0.20 gram each, into two 200 cc. lipped beakers. Pour over them 20 cc. of nitric acid (sp. gr. 1.2), and warm gently until solvent action has apparently ceased. Unless the absence of soluble silicates is assured, evaporate the solution cautiously to dryness, heat the residue for about an hour at 120–130° C., and treat it again with nitric acid as described above; separate the residue of silica by filtration on a small filter (7 cm.) and wash with warm water, using as little as possible. Receive the filtrate in a 300 or 500 cc. lipped beaker. Test the washings with ammonia for calcium phosphate, but add all such tests in which a precipitate appears to the original filtrate. The filtrate and washings should not exceed 100 cc. in volume. Add aqueous ammonia until the precipitate of calcium phosphate first produced just fails to redissolve, and then add a few drops of nitric acid until this is again brought into solution. Warm the solution until it cannot be comfortably held in the hand, and after removal from the lamp add 75 cc. of ammonium molybdate solution (68 grams MoO_3 per liter) which has been *gently* warmed, but which must be perfectly clear. Allow the mixture to stand at a temperature of about 50° to 60° C. for twelve hours. Filter off the yellow precipitate on a 9 cm. filter, and wash by decantation with a solution of ammonium nitrate made acid with nitric acid.[1] Allow the precipitate to remain in the beaker as far as possible. Test the washings for calcium with ammonia and ammonium oxalate.

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[1] This solution is prepared as follows: Mix 100 cc. of ammonia solution (sp. gr. 0.96) with 325 cc. of nitric acid (sp. gr. 1.2), and dilute with 100 cc. of water.

Add 10 cc. of molybdate solution to the filtrate, and leave it for a few hours. It should then be carefully examined for a *yellow* precipitate; a white precipitate may be neglected. The filtrate should not be thrown away, but should be placed in a suitable receptacle for "molybdenum residues" (from which the molybdic acid may be ultimately recovered, if desired).

Dissolve the precipitate upon the filter by pouring through it dilute aqueous ammonia (one volume of ammonia [sp. gr. 0.96] and three volumes water, which should be *carefully measured*), and receive the solution in the beaker containing the bulk of the precipitate. The total volume of filtrate and washings must not exceed 100 cc.

Calculate the volume of magnesium ammonium chloride solution ("magnesia mixture") required to precipitate the phosphoric acid, assuming 40 per cent. P_2O_5 in the apatite. Measure out about 5 cc. in excess of this amount, and pour this very slowly into the ammoniacal solution, with constant stirring. Continue the stirring for a few moments, and set the solution aside for some hours, best over night. (If it is desired to hasten the precipitation, the solution may be cooled by immersion in ice water and stirred *constantly* for a half hour, when precipitation will usually be complete.) Decant the clear liquid through a filter and wash the precipitate on to the filter, using a mixture of one volume ammonia solution (sp. gr. 0.96) to three volumes of water, but do not attempt to clean the beaker completely. Dissolve the precipitate from the filter in a little hydrochloric acid (sp. gr. 1.12), allowing the acid solution to run into the beaker in which the original precipitation was made. Wash the filter with water until the wash-water shows no test for chlorides, but avoid an unnecessary amount of wash-water. Add to the solution 2 cc. (not more) of magnesia mixture, and then ammonium hydroxide solution (sp. gr. 0.96), drop by drop, with constant stirring, until the liquid smells distinctly of ammonia. Stir for a few moments and then add a volume of ammonia water (sp. gr. 0.96) equal to one-third of the volume of the solution. Allow

the solution to stand for some hours, and then filter off the magnesium ammonium phosphate, which should be distinctly crystalline in character. Wash the precipitate with dilute ammonia water, as prescribed above, until finally 3 cc. of the washings, after acidifying with nitric acid, show no evidence of chlorides. Test both filtrates for complete precipitation by adding a few cubic centimeters of magnesia mixture and allowing them to stand for some time.

Cover the funnel with a paper, dry the filter completely in the drying closet, and then ignite, using great care to raise the temperature slowly and to insure the presence of plenty of oxygen during the combustion of the filter paper, thus guarding against a possible reduction of the phosphate, which would result in disastrous consequences both to crucible and analysis. Do not raise the temperature above moderate redness until the precipitate is *white*. (Keep this precaution well in mind.) Ignite finally at the highest temperature of the Tirrill burner, and repeat the heating until the weight is constant. From the weight of magnesium pyrophosphate ($Mg_2P_2O_7$) obtained, calculate the weight of phosphoric anhydride (P_2O_5) and the percentage of the latter in the sample of apatite.

Notes.—1. Apatite may contain, besides calcium phosphate, either calcium fluoride or chloride. It is evident that the direct precipitation of the phosphoric acid in combination with magnesium is impracticable in the presence of any metal which forms compounds with phosphoric acid which are insoluble in ammoniacal liquids; such, for example, as iron, aluminium, chromium, and the alkaline earths. The previous isolation of the phosphoric acid in combination with molybdenum, which can be effected in nitric acid solution as described, is then necessary.

2. As a result of the slight solubility of magnesium ammonium phosphate, as noted below, the unavoidable errors of analysis are greater in this determination than in those which have preceded it, and some divergence may be expected in duplicate analyses. It is obvious that the larger the amount

of substance taken for analysis the less will be the relative loss or gain due to experimental errors; but in this instance a check is placed upon the amount of material which may be taken, both by the bulk of the resulting precipitate of ammonium phospho-molybdate and by the excessive amount of ammonium molybdate required to effect complete separation of the phosphoric acid, since a liberal excess above the theoretical quantity is demanded. Molybdic acid is one of the more expensive reagents.

3. Soluble silicic acid might, if present, partially separate with the phospho-molybdate, although not in combination with molybdenum. Its previous removal by dehydration is therefore necessary.

4. Nitric acid is chosen as a solvent because the phospho-molybdate is slightly soluble in hydrochloric acid. An excess of nitric acid also exerts a slight solvent action, while ammonium nitrate lessens the solubility; hence the neutralization of the former by ammonia.

5. The composition of the "yellow precipitate" undoubtedly varies slightly with varying conditions at the time of its formation. Its composition may probably be represented by the formula, $(NH_4)_3PO_4.12MoO_3.H_2O$, when precipitated under the conditions prescribed in the procedure. Whatever other variations may occur in its composition, the ratio of $12MoO_3 : 1P$ seems to hold; and this fact is utilized in volumetric processes for the determination of phosphorus, in which the molybdenum is reduced to a lower oxide and reoxidized by a standard solution of potassium permanganate.

6. The precipitation of the phospho-molybdate takes place more promptly in warm than in cold solutions, but the temperature should not exceed 60° C. during precipitation; a higher temperature tends to separate molybdic acid from the solution. This acid is nearly white, and its deposition in the filtrate on long standing should not be mistaken for a second precipitation of the yellow precipitate. The addition of 75 cc. of ammonium molybdate solution insures the presence of a liberal excess of the reagent.

The precipitation is probably complete in many cases in less than twelve hours; but it is better, when practicable, to allow the solution to stand for this length of time.

Vigorous shaking or stirring promotes the separation of the precipitates.

7. When washing the siliceous residue the filtrate may be tested for calcium by adding ammonia alone, since that reagent neutralizes the acid which holds the calcium phosphate in solution and causes precipitation; but after the removal of the phosphoric acid in combination with the molybdenum, the addition of an oxalate is required to show the presence of calcium.

8. Magnesium ammonium phosphate is not a wholly insoluble substance, even under the most favorable analytical conditions. It is least soluble in a liquid containing one-fourth of its volume of aqueous ammonia (sp. gr. 0.96), and this proportion should be carefully maintained as prescribed in the procedure. On account of this slight solubility the volume of solutions should be kept as small as possible and the amount of wash-water limited to that absolutely required.

9. A large excess of the magnesium solution tends both to throw out magnesium hydroxide (shown by a persistently flocculent precipitate) and to cause the phosphate to carry down molybdic acid. The latter should have been removed by the reprecipitation of the magnesium precipitate, but if its presence is suspected it may be removed from the phosphate by dissolving the precipitate in hydrochloric acid and passing sulphureted hydrogen through the warm solution from three to four hours.

The tendency of the magnesium precipitate to carry down molybdic acid is greater if the solution is too concentrated. The volume should not be less than 90 cc. nor more than 125 cc. at the time of the first precipitation with the magnesia mixture.

10. The magnesium ammonium phosphate should be perfectly crystalline, and will be so if the directions are followed. The slow addition of the reagent is essential, and the stirring not less so. Stirring promotes the separation of the precipitate and the formation of larger crystals, and may therefore be substituted for digestion in the cold. The stirring rod must not be allowed to scratch the glass, as the crystals adhere to such scratches and are removed with difficulty.

The remarks on page 7 regarding the formation of large

crystals by digestion with the solution have peculiar force in connection with the magnesium ammonium phosphate, which is a *relatively* soluble body.

The reprecipitation of the magnesium precipitate may not always be necessary, but it is usually advisable, since the first precipitate is likely to contain some magnesium hydroxide and some molybdic acid, which are removed by this procedure.

The conditions for final precipitation are most favorable when ammonia is present in slight excess during the separation. A considerable excess is added after the precipitation is practically complete.

11. During ignition the magnesium ammonium phosphate loses ammonia and water and is converted into magnesium pyrophosphate.

$$2NH_4MgPO_4 = Mg_2P_2O_7 + 2NH_3 + H_2O.$$
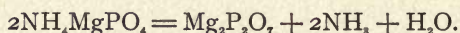
The precautions mentioned on page 11 must be observed with great care during the ignition of this precipitate. The danger here lies in a possible reduction of the phosphate by the carbon of the filter paper, or by the ammonia evolved, which may act as a reducing agent. The phosphorus then attacks and injures the crucible, and the determination is valueless.

If extreme care is employed, it is possible to ignite this precipitate without previous drying; but the student is not advised to attempt this until some general experience has been gained.

12. The ionic change which takes place in the reaction between the phosphoric acid and the ammonium molybdate is complicated, and cannot be stated with exactness. That involved in the precipitation of the magnesium compound is $PO_4^{---} + NH_4^+ + Mg^{++} = \mathbf{MgNH_4PO_4}$. The magnesium ammonium phosphate is readily dissolved by acids, even those which are no stronger than acetic acid. This is accounted for by the fact that two of the ions into which phosphoric acid may dissociate, the HPO_4^{--} or $H_2PO_4^-$-ions, exhibit the characteristics of very weak acids, in that they show almost no tendency to dissociate further into H^+ and PO_4^{---}-ions. Consequently the ionic changes which occur when the mag-

nesium ammonium phosphate is brought into contact with an acid may be typified by the reaction, $H^+ + Mg^+ + NH_4^+ + PO_4^{---} = Mg^+ + NH_4^+ + HPO_4^{--}$; that is, the PO_4^{---}-ions and the H^+-ions lose their identity in the formation of the new ion, HPO_4^{--}, and this continues until the magnesium ammonium phosphate is entirely dissolved.

The ignited magnesium pyrophosphate may, in case its purity is questioned, be redissolved in nitric acid and again precipitated by the addition of ammonium hydroxide and a little magnesia mixture. In dissolving the precipitate a moderate excess of nitric acid is employed, and the solution heated about four hours on the water bath in order to reconvert the pyrophosphoric acid into orthophosphoric acid. $H_4P_2O_7 + H_2O = 2H_3PO_4$.

ANALYSIS OF LIMESTONE

Limestones vary widely in composition from a nearly pure marble through the dolomitic limestones, containing varying amounts of magnesium, to the impure varieties, which contain also ferrous and manganous carbonates and siliceous compounds in considerable proportions. In nearly all varieties there will be found a siliceous residue insoluble in dilute acids, of which account must be taken in analyses.

SELECTION OF THE SAMPLE

Procedure.—If the material for analysis is in the form of lumps, it should be carefully examined and pieces broken from different lumps, amounting to 20 or 30 grams in all. These must be selected with a view to obtaining a representative sample. Crush these lumps in a steel mortar until all of the powder will pass a 60-mesh sieve, as some ingredients may be harder or softer than others. Mix this material thoroughly by turning it over on a large sheet of clean paper, using a spatula. To determine the moisture, transfer about 25 grams of the powder to a weighing beaker (with a ground-glass stopper) and heat at 105° C.; and after cooling in a desiccator, weigh at intervals of an hour, until the loss of weight after an hour's heating does not exceed 10 milligrams. Remove the stopper of the weighing beaker during the heating, but stopper it during cooling and weighing.

Fill a weighing-tube for analysis from the portion of the powdered sample not used for the moisture determination.

DETERMINATION OF THE INSOLUBLE MATTER AND SILICA

Procedure.—Weigh out two portions of about 5 grams each into 250 cc. casseroles, and cover each with a watch-glass. Pour over the powder 25 cc. of water, and then add 50 cc. hydrochloric acid (sp. gr. 1.12) in small portions, warming gently, until nothing further appears to dissolve. Evaporate to dryness on the water bath. Pour over the residue a

mixture of 5 cc. of water and 5 cc. of hydrochloric acid (sp. gr.
1.2) and again evaporate to dryness, and finally heat for at
least an hour at a temperature about 120° C. Pour over this
residue 50 cc. of dilute hydrochloric acid (one volume acid
[sp. gr. 1.12] to five volumes water), and boil for about five
minutes; then filter and wash twice with the dilute hydro-
chloric acid, and then with hot water until free from chlorides.
Transfer the filter and contents to a platinum crucible, dry
carefully over a low flame, and ignite to constant weight.
The residue represents the insoluble matter and the silica
from any soluble silicates (see Note 2). Calculate the per-
centage of these in the limestone.

DETERMINATION OF FERRIC OXIDE AND ALUMINA (WITH
MANGANESE)

Procedure.—To the filtrate from the insoluble residue add
10 cc. of ammonium chloride solution and ammonium hydrox-
ide until the solution smells strongly of ammonia. Then add
5 cc. of bromine water and boil for five minutes, adding
ammonium hydroxide if the odor of ammonia disappears.
Warm until the hot solution barely smells of ammonia, allow
it to stand for a few moments, and filter promptly. Wash
the filter twice with hot water, then pour through it 25 cc. of
hot, dilute hydrochloric acid (one volume HCl [sp. gr. 1.12]
to five volumes water). A brown residue insoluble in the acid
may be allowed to remain on the filter. Wash the filter five
times with hot water, add to the filtrate ammonium hydroxide
and bromine water as described above, and repeat the precipi-
tation. Collect the precipitate on the filter already used, wash
it free from chlorides with hot water, and ignite and weigh
as described for ferric hydroxide on page 28. The residue
after ignition consists of ferric oxide, alumina, and mangano-
manganic oxide (Mn_3O_4) if manganese is present. These
are commonly determined together (see Note 4, page 50).
Calculate the percentage of the combined oxides in the
limestone.

DETERMINATION OF CALCIUM

Procedure.—To the combined filtrates from the double precipitation just described, add 5 cc. of ammonium hydroxide (sp. gr. 0.96), and transfer the liquid to a 500 cc. graduated flask, washing out the beaker carefully, noting the suggestions on page 6. Cool to laboratory temperature, and fill the flask with distilled water until the lowest point of the meniscus is exactly level with the mark on the neck of the flask. Carefully remove any drops of water which are on the inside of the neck of the flask above the graduation by means of a strip of filter paper, make the solution uniform by pouring it out into a dry beaker and back into the flask several times, and finally stopper the flask. Measure off one-fifth of this solution as follows: Pour into a 100 cc. graduated flask about 10 cc. of the solution, shake the liquid thoroughly over the inner surface of the small flask, and pour it out. Repeat the same operation. Fill the 100 cc. flask until the lowest point of the meniscus is exactly level with the mark on its neck, remove any drops of solution from the upper part of the neck with filter paper, and pour the solution into a beaker of about 400 cc. capacity. Wash out the flask with small quantities of water until it is clean, adding these to the main solution. (Consult also note on page 50.) When the portion of 100 cc. is measured out from the duplicate solution, remember that the flask must be rinsed out twice with that solution, as prescribed above, before the final measurement is made.

Dilute the solution to 250 cc. with distilled water, heat it to boiling, and add ammonium oxalate solution slowly in moderate excess, stirring well. Boil for two minutes, allow the precipitated calcium oxalate to settle for a half hour, and decant through a filter. Test the filtrate for complete precipitation by adding a few cubic centimeters of the precipitant, allowing it to stand for fifteen minutes. If no precipitate forms, make the solution slightly acid with hydrochloric acid, and proceed with the magnesium determination.

Redissolve the calcium oxalate in the beaker with warm

hydrochloric acid, pouring the acid through the filter. Wash the filter five times with water, and finally pour through it aqueous ammonia. Dilute the solution to 250 cc., bring to boiling, and add 1 cc. ammonium oxalate solution and ammonia in slight excess; boil for two minutes, and set aside for a half hour. Filter off the calcium oxalate upon the filter first used, and wash free from chlorides. The filtrate should be made barely acid and combined with the first filtrate.

The precipitate of calcium oxalate may be ignited without drying, and, after burning the filter, it should be ignited for three-quarters of an hour at the highest heat of the Bunsen or Tirrill burner, and finally for three minutes at the blast lamp. Repeat until the weight is constant. As the calcium oxide absorbs moisture from the air, it must (after cooling) be weighed as rapidly as possible. (Compare Note 8, on page 30.) From the weight of the oxide calculate the weight of calcium and the percentage of the latter in the limestone, remembering that only one-fifth of the total solution is used for this determination.

Barely acidify the filtrate from the calcium oxalate with hydrochloric acid, and proceed with the magnesium determination.

DETERMINATION OF MAGNESIUM

Procedure.—Evaporate the acidified filtrates from the calcium precipitates until the salts begin to crystallize, but do *not* evaporate to dryness. Dilute the solution cautiously until the salts are brought into solution, adding a little acid if the solution has evaporated to very small volume. The solution should be carefully examined at this point and must be filtered if it contains insoluble matter. Add to the clear solution ammonia water (sp. gr. 0.96) until it smells distinctly of ammonia, but do not add an excess. Add di-sodium phosphate solution, drop by drop, as long as a precipitate continues to form, and then add 10 cc. in excess. Finally, add one-third of the total volume of ammonia water (sp. gr. 0.96), and allow the solution to stand over night (or about twelve

hours). Decant the solution through a filter, wash it with dilute ammonia water, proceeding as prescribed for the determination of phosphoric anhydride on page 38, except that 3 cc. of di-sodium phosphate solution are added before the reprecipitation of the magnesium ammonium phosphate instead of the magnesia mixture there prescribed. Remember that the pyrophosphate finally obtained is from one-fifth of the original sample.

Notes.—1. When the general characteristics of a limestone are not accurately known, a qualitative analysis should always precede the quantitative examination, and particular attention should be paid to the indications of the presence of manganese and to the nature of the insoluble residue, especially with reference to its calcium contents. If manganese is absent, or present only in minute amounts, the second addition of the bromine recommended on page 45 may be omitted; and if the residue is essentially silica, or insoluble silicates, it may often be weighed and determined as a whole, as prescribed above, without further examination. If, however, it is desired to determine the percentage of silica separately, the ignited residue should be mixed in a platinum crucible with about six times its weight of anhydrous sodium carbonate, and the procedure given on page 71 for insoluble silicates should be followed. The filtrate from the silica is then added to the main filtrate from the insoluble residue.

It is plain that the amount of the insoluble residue and also its character will often depend upon the strength of acid used for solution of the limestone. It cannot, therefore, be regarded as representing any well-defined constituent, and its determination is essentially empirical.

The procedure as given here makes no provision for the determination of sulphur, phosphorus, titanium, the alkali metals, or organic matter, which may be present in certain limestones. These require special methods, and reference should be made to the admirable description of a complete analysis of a limestone given by Dr. W. F. Hillebrand in Bulletin No. 305 of the United States Geological Survey.

A relatively large weight (5 grams) when taken for analysis insures greater accuracy in the determination of the ingredients which are present in small proportions, and is also more likely to be a representative sample of the material analyzed.

2. The determination of moisture is not always necessary in practice, as the results are often reported upon the air-dried sample. When, however, it is desired to make the dried sample the basis of analysis, all results must be corrected for the percentage of moisture found.

It may occasionally happen that hydrous silicates are present in the limestone, and on ignition of the residue these lose water of constitution; the percentage of insoluble residue found is then below the true value on this account. Where it is essential to obtain correct values, the insoluble residue may be collected on a previously weighed paper filter, dried at 105° C., and weighed.

3. It is probable that some of the silicates present are wholly or partly decomposed by the acid, and the soluble silicic acid must be removed by evaporation to dryness and heating, which changes it to insoluble silica. This change is not complete after one evaporation. The heating at a temperature somewhat higher than that of the water bath for a short time tends to leave the silica in the form of a powder, which promotes subsequent filtration. The siliceous residue is washed first with dilute acid to prevent hydrolytic changes, which would result in the formation of appreciable quantities of basic iron or aluminium salts on the filter when washing with hot water.

4. The addition of bromine water to the ammoniacal solution serves to oxidize any ferrous hydroxide to ferric hydroxide and to precipitate manganese as $MnO(OH)_2$. The solution must not contain more than a bare excess of hydroxyl ions (ammonium hydroxide) when it is filtered, on account of the tendency of the aluminium hydroxide to redissolve.

If a separate determination of the iron, aluminium, and manganese is desired, the mixed precipitate may be dissolved in acid before ignition, and the separation effected by special methods (see, for example, Treadwell-Hall, *Analytical Chemistry*, Vol. II, pp. 121–124).

In the absence of significant amounts of manganese the iron and aluminium may be separately determined by fusion of the mixed ignited precipitate, after weighing, with about ten times its weight of acid potassium sulphate, solution of the cold fused mass in water, and volumetric determination of the iron as described on page 120. The aluminium is then determined by difference, after subtracting the weight of ferric oxide corresponding to the amount of iron found.

5. The precipitate produced by ammonium hydroxide and bromine should be filtered off promptly, since the alkaline solution absorbs carbon dioxide from the air, with consequent partial precipitation of the calcium as carbonate. This is possible even under the most favorable conditions, and for this reason the iron precipitate is redissolved and again precipitated to free it from calcium. When the precipitate is small and extreme accuracy is not essential, this reprecipitation may be omitted.

6. If the calcium were precipitated from the entire solution, the quantity of the precipitate would be greater than could be properly treated. The solution is, therefore, diluted to a definite volume (500 cc.), and exactly one-fifth (100 cc.) is measured off. To attain this end it is evident that the solution must be thoroughly uniform, which is brought about by careful mixing, and that it must not be diluted by water adhering to the small flask. This is insured by rinsing out this flask several times with the solution, instead of drying it, which would consume much time. The two flasks must be graduated at the same temperature, and if, as is usual, the small flask is graduated to contain 100 cc., it must be rinsed out with water before all the calcium and magnesium belonging to one-fifth of the solution are obtained. This, and other kindred considerations, are discussed under Volumetric Analysis. A pipette might properly be substituted for the small flask, if desired.

7. The accurate quantitative separation of calcium and magnesium as oxalates requires considerable care. The calcium precipitate usually carries down with it some magnesium, and this can best be removed by redissolving the precipitate after filtration and reprecipitation in the presence of only the small amount of magnesium which was

included in the first precipitate. When, however, the proportion of magnesium is not very large, the second precipitation of the calcium can usually be avoided by precipitating it from a rather dilute solution (800 cc. or so) and in the presence of a considerable excess of the precipitant; that is, rather more than enough to convert both the magnesium and calcium into oxalates.

8. The small quantity of ammonium oxalate solution is added before the second precipitation of the calcium oxalate to insure the presence of a slight excess of the reagent, which promotes the separation of the calcium compound. (See Note 11.)

9. On ignition the calcium oxalate loses carbon dioxide and carbon monoxide, leaving calcium oxide.

$$CaC_2O_4 = CaO + CO_2 + CO.$$
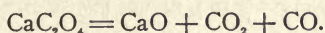
For small weights of the oxalate (0.5 gram or less), this reaction may be brought about at the highest temperature of a Tirrill burner, but it is well to ignite larger quantities than this over the blast lamp until the weight is constant.

The calcium oxalate may be converted into calcium sulphate, and weighed as such, by adding 2 cc. of dilute sulphuric acid to the crucible, after burning off the filter, and cautiously heating to remove the excess of acid. The sulphate is then heated over the Bunsen burner during five-minute intervals until the weight is constant. This procedure is preferred by many analysts. The reaction involved is $CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2O + CO_2 + CO$.

10. The filtrate from the calcium oxalate should be made slightly acid immediately after filtration, in order to avoid the solvent action of the alkaline liquid upon the glass.

11. The ionic changes involved in the precipitation of calcium as oxalate are exceedingly simple, and the principles discussed in connection with the barium sulphate precipitation on page 33 also apply here. $C_2O_4^{--} + Ca^{++} = CaC_2O_4$.

Calcium oxalate is nearly insoluble in water, and only very slightly soluble in acetic acid, but is readily dissolved by the strong mineral acids. This behavior with acids is explained by the fact that oxalic acid is a stronger acid than

acetic acid; when, therefore, the oxalate is brought into contact with the latter there is almost no tendency to diminish the concentration of $C_2O_4^{--}$-ions by the formation of an acid less dissociated than the acetic acid itself, and practically no solvent action ensues. When a strong mineral acid is present, however, the ionization of the oxalic acid is much reduced by the high concentration of the H^+-ions from the strong acid, the formation of the undissociated acid lessens the concentration of the $C_2O_4^{--}$-ions in solution, more of the oxalate passes into solution to reëstablish equilibrium, and this process repeats itself until all is dissolved. $C_2O_4^{--} + 2H^+ = (C_2H_2O_4)$.

The oxalate is immediately reprecipitated from such a solution on the addition of OH^--ions, which, by uniting with the H^+-ions of the acids (both the mineral acid and the oxalic acid) to form water, leave the Ca^{++} and $C_2O_4^{--}$-ions in the solution to recombine to form **CaC_2O_4**, which is precipitated in the absence of the H^+-ions. It is well at this point to add a small excess of $C_2O_4^{--}$-ions in the form of ammonium oxalate to decrease the solubility of the precipitate. (See Appendix.)

The oxalate precipitate consists mainly of $CaC_2O_4.H_2O$ when thrown down. It loses the water of crystallization at about 205° C., and at low redness is changed to $CaCO_3$, and may, with due precaution, be weighed as such; but complete conversion to the oxide by strong ignition, or to the sulphate, is generally to be preferred.

12. The precipitation of the magnesium should be made in as small volume as possible, and the ratio of ammonia to the total volume of solution should be carefully provided for, on account of the relative solubility of the magnesium ammonium phosphate. This matter has been fully discussed in connection with the phosphoric anhydride determination. (Compare Note 8, page 41.)

13. The first magnesium ammonium phosphate precipitate is rarely wholly crystalline, as it should be, and is not always of the proper composition when precipitated in the presence of such large amounts of ammonium salts. The difficulty can be best remedied by filtering the precipitate and (without washing it) redissolving in a small quantity of hydrochloric

acid, from which it may be again thrown down by ammonia after adding a little of di-sodium phosphate solution. If the flocculent character was occasioned by the presence of magnesium hydroxide, the second precipitation, in a smaller volume containing fewer salts, will often result more favorably.

The removal of iron or alumina from a contaminated precipitate is a matter involving a long procedure, and a redetermination of the magnesium from a new sample, with additional precautions, is usually to be preferred.

DETERMINATION OF CARBON DIOXIDE

The apparatus required for the determination of the carbon dioxide should be previously arranged as shown in the cut (Fig. 2). The flask A is arranged as an ordinary washbottle, in which should be placed 50 cc. of hydrochloric acid (sp. gr. 1.12) and 100 cc. of water. This flask is connected by rubber tubing with the tube (b) leading nearly to the bottom of the evolution flask (B) and having its lower end bent upward to avoid loss of gas. The evolution flask may conveniently be a wide-mouthed Soxhlet extraction flask of about 150 cc. capacity, the mouth of which is fitted with a double-bored rubber stopper. C is a ball-condenser (or may be a small glass [Liebig] condenser), from the top of which a delivery-tube leads to the U-tube (D), containing some glass beads and 3 cc. of a saturated solution of silver sulphate with 3 cc. of concentrated sulphuric acid. The second tube (E) is filled with calcium chloride, and should have a small, loose plug of cotton at the top of each arm. Both tubes should be closed by cork stoppers, the tops of which are sunk slightly below the top of the U-tube, and then neatly sealed with sealing wax.

The Geissler bulb (F) should be so filled with potassium hydroxide solution (sp. gr. 1.27) that each small bulb is about two-thirds full. There should be attached to the bulb, in such a manner that it can be weighed with it, a filled calcium chloride tube (3 in.). A platinum wire should be attached to the bulb to permit it to hang upon the support.

An additional U-tube, to be used as a safety tube (H), should be filled with soda-lime ready for use.

When the apparatus is ready, weigh out into the flask (B) about 1.0 gram of the limestone and cover it with 15 cc. of water. Carefully wipe the Geissler bulb (F), with its calcium chloride prolong tube, and weigh accurately. Afterward stopper the openings by means of small pieces of rubber tubing closed by pieces of glass rod.
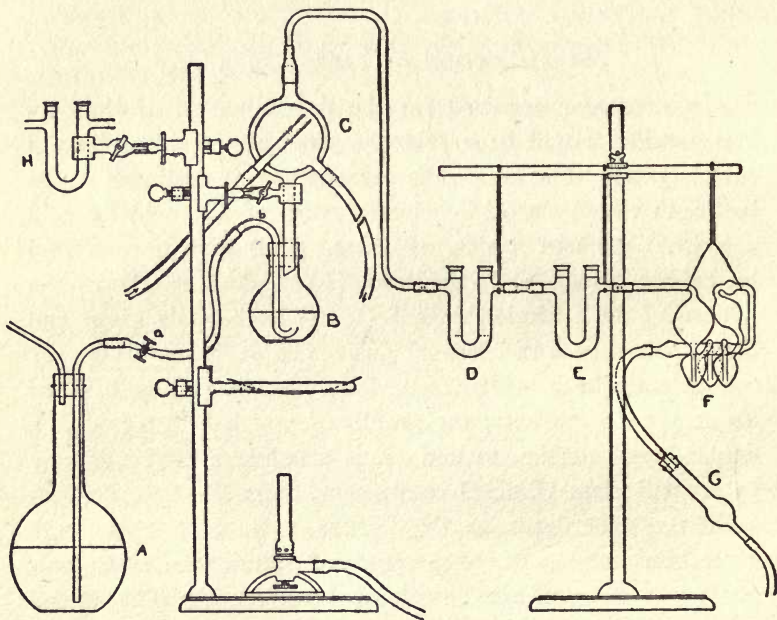
Fig. 2

Place the flask (B) on the apparatus, making sure that the stopper fits tightly, and connect the Geissler bulb with the U-tubes; disconnect the rubber tube from A, close the pinch-cock (a), apply suction at the end of the Geissler bulb, and note whether the apparatus is absolutely air-tight. This precaution must not be neglected, and care must afterward be taken to admit air slowly by cautiously opening (a) to equalize the pressure. The rubber tube must, of course, contain no hydrochloric acid at this time.

When it is certain that the apparatus is ready for use, connect the rubber tube with the flask (*A*), and, opening the pinch-cock (*a*), blow over about 10 cc. of the diluted acid. When the evolution of carbon dioxide slackens add a fresh portion of acid. The gas should not enter the Geissler bulb more rapidly than two bubbles per second. When the action of the acid ceases in the cold, run water through the condenser (*C*) and apply a small flame to the flask, cautiously bringing the liquid to the boiling point, and continue to boil it slowly for about three minutes. Replace the flask (*A*) by the safety tube (*H*). Apply suction at the end of the Geissler bulb, and regulate it in such a way that when the pinch-cock (*a*) is opened the air will pass slowly through the apparatus, the rate not to exceed that named above. Do not remove the lamp from under the flask (*B*) until the air current is adjusted. Continue to draw air through the apparatus from twenty to thirty minutes; then disconnect the Geissler bulb, stopper it, place it in the balance room, and after an interval of thirty minutes wipe it carefully and weigh it without the stoppers. The increase in weight is due to absorption of carbon dioxide. Repeat the determination with a fresh portion of limestone.

Notes.—1. By very cautious procedure it is possible to avoid the use of a condenser above the evolution flask, or a tube with one or two bulbs blown in it may be substituted. More moisture is then likely to be carried over into the U-tubes, which soon require refilling. The use of a condenser is, therefore, preferable.

2. The air current may carry minute quantities of hydrochloric acid through the apparatus. This acid is retained by the silver sulphate solution in the first U-tube. The beads serve to divide the bubbles of gas as they pass through the liquid. The sulphuric acid lessens the evaporation of the silver sulphate solution.

The calcium chloride in the second tube assures the removal of the water from the moisture-laden air from the evolution flask. As calcium chloride frequently contains

basic salts, which would retain carbon dioxide, it is necessary to pass a current of that gas through the U-tube for a short time, and follow this by a current of dry air for thirty minutes before using the tube.

3. The essential ionic changes involved in this procedure are the following: It is assumed that the limestone, which is typified by calcium carbonate, is very slightly soluble in water, and the ions resulting are Ca^{++} and CO_3^{--}. In the presence of the H^+-ions of the mineral acid, the CO_3^{--}-ions form H_2CO_3, which is not only a weak acid (and by its formation diminishes the concentration of the CO_3^{--}-ions, thus causing more of the carbonate to dissolve to reëstablish equilibrium), but is also an unstable compound, and breaks down into carbon dioxide and water. The carbon dioxide on coming into contact with the potassium hydroxide forms potassium carbonate. $CO_2 + 2K^+ + 2OH^- = 2K^+ + CO_3^{--} + (H_2O)$, or $CO_2 + 2OH^- = CO_3^{--} + (H_2O)$.

After the potassium hydroxide is approximately half consumed in the first bulb of the absorption apparatus, potassium bicarbonate is formed, and as it is much less soluble than the carbonate, it often precipitates. Its formation is a warning that the absorbing power of the hydroxide is much diminished. The ionic changes are, then: $CO_2 + K^+ + OH^- = \mathbf{KHCO_3}$.

4. The solution of the hydroxide must be highly concentrated to insure complete absorption of the carbon dioxide and also to reduce the vapor pressure of the solution, thus lessening the danger of loss of water with the air which passes through the bulbs. The small quantity of moisture which is then carried out of the bulbs is held by the calcium chloride in the prolong tube. The best form of absorption bulb is that to which the prolong tube is attached by a ground-glass joint.

5. Carbon dioxide is dissolved by cold water, but the gas is expelled by boiling, and, together with that which is distributed through the apparatus, is swept out into the absorption bulb by the current of air. This air is purified by drawing it through the tube (H) containing soda-lime, which removes any carbon dioxide which may be in the atmosphere.

6. Instead of the potassium hydroxide in a Geissler bulb,

soda-lime, which should be placed in two U-tubes with suitable device for weighing, may be employed to absorb the carbon dioxide. Soda-lime is a mixture of sodium and calcium hydroxides, and unites with the gas to form carbonates. Some care is necessary to guard against loss of moisture from the soda-lime, as considerable heat is generated during the absorption.

7. Great care is necessary when the suction is applied to avoid a violent passage of gas through the apparatus and to prevent regurgitation.

It is advisable to interpose a tube (G) containing calcium chloride and soda-lime between the suction tube and the potash bulb to prevent possible contamination of the latter.

8. The large surface presented to the air by the Geissler bulbs admits of the accumulation of dust and moisture during the determination. They must, therefore, be cautiously cleaned before each weighing by wiping with a clean, lintless cloth or a piece of wash leather. They should stand for thirty minutes near the balance to assure uniformity of temperature, any change of which at the second weighing of so large an object might cause an appreciable error.

The stoppers should be removed from the bulbs on weighing, that the air inclosed may be at atmospheric pressure.

9. The procedure described above for the determination of carbon dioxide is capable of yielding accurate results, but is somewhat slow. There are more rapid methods, most of which depend upon the loss of weight which results from the evolution of the carbon dioxide when a limestone is treated with concentrated sulphuric acid, and many special pieces of apparatus have been designed for use in this process. The results are obtained quickly and are sufficiently accurate for many purposes. (See, for example, Treadwell-Hall, *Quantitative Analysis,* Vol. II, p. 293.)

DETERMINATION OF LEAD, COPPER, AND ZINC IN BRASS

DETERMINATION OF LEAD

Procedure.—Select clean, bright chips or borings, or, if the brass is in the form of wire, polish a piece of suitable size by rubbing with emery, cleaning it carefully afterward. Weigh out two portions of about 5 grams each, and dissolve them in covered casseroles in 50 cc. of nitric acid (sp. gr. 1.2). When the solution is complete, cool, wash off the cover glass, and add slowly 10 cc. of sulphuric acid (sp. gr. 1.84). Evaporate under a hood until heavy white fumes of sulphuric anhydride are evolved, keeping the casserole well covered meanwhile; cool, add 75 cc. of water, boil until the sulphates of copper and zinc have dissolved, and set the solution aside for an hour. Filter off the lead sulphate, wash it by decantation with dilute sulphuric acid (one volume of concentrated acid to five volumes of water) until the washings are free from copper, as shown by the ammonia test. Set the filtrate aside for the determination of copper and zinc, and transfer the lead sulphate to the filter, finally washing the filter with alcohol diluted with an equal volume of water until free from sulphuric acid. Be sure that all the sulphate is removed from the casserole. Discard the alcoholic washings, if they are entirely clear. Dry the filter, and, if practicable, separate the lead sulphate from it, as described on page 21. Prepare a No. 7 porcelain crucible for use by heating and weighing, burn the filter on a platinum wire as described on page 21, and when cold add to the ash two drops of nitric acid (sp. gr. 1.42), warm gently, and then add one drop of sulphuric acid. Ignite with great care until the acids are expelled. Transfer to the crucible the precipitate which was separated from the filter, and ignite at a moderate red heat. Repeat the heating until the weight is constant.

From the weight of the lead sulphate calculate the weight of lead and the percentage of the latter in the brass.

*Notes.—*1. It is obvious that the brass taken for analysis should be untarnished, which can be easily assured, when wire is used, by scouring with emery. If chips or borings are used, they should be well mixed, and the sample for analysis taken from different parts of the mixture.

2. The small percentage of lead usually found in brasses makes it necessary to weigh out a considerable quantity in order to secure accuracy. The amount taken (5 grams) is too large to use directly for the determination of copper and zinc on account of the bulk of the precipitates which would then have to be handled. An aliquot part of this filtrate is, therefore, used for these analyses, as noted under the determination of copper.

3. Lead sulphate is slightly soluble in nitric acid; hence the latter is removed by heating with sulphuric acid until the more volatile acid is expelled. This point is indicated by the appearance of the heavy, white fumes.

4. The sulphuric acid of the wash-water, if allowed to remain on the filter, would char it during the drying, making subsequent handling difficult or impossible. It is accordingly removed by washing with dilute alcohol in which the sulphate is insoluble; but the alcohol is not added to the main filtrate, as its presence is not advantageous during the subsequent operations.

5. The lead sulphate must be separated from the filter for the same reasons which apply in the case of silver chloride. (Compare page 22.) The addition of nitric acid to the ash dissolves any reduced lead, and the sulphuric acid converts it to sulphate. A slight loss of lead is possible if the reduction of any considerable quantity of the precipitate takes place, and it is evident that the ignition of this precipitate in platinum is impracticable.

6. It is possible to determine the percentage of lead in the brass by solution in nitric acid, partial neutralization of the excess of acid, and deposition of the lead by an electric current as peroxide (PbO_2) on the anode; but the relatively large percentage of copper makes the simultaneous determination of that element difficult, if a sufficiently large quantity of the brass be taken for analysis to also secure an accurate determination of the lead. For the determination of

small quantities of lead alone, this method may well be employed.

7. Lead sulphate is soluble in about 31,500 parts of water at 15° C., but it is less soluble in dilute sulphuric acid, as would be expected on account of the greater concentration of the SO_4^{--}-ions in the latter. With the increasing concentration of the sulphuric acid, however, the solubility again increases and the sulphate is relatively soluble in concentrated sulphuric acid, the compound in solution being stated to have the composition $PbH_2(SO_4)_2$. The sulphate is also quite soluble in concentrated hydrochloric or nitric acid, which may very likely be due to the lessened dissociation of the sulphuric acid formed on solution of the sulphate in the presence of the H^+-ions of the other acids, and the consequent lessening of the concentration of the SO_4^{--}-ions; and it is also possible that the formation of a complex anion containing lead aids in the solution of the sulphate, as such anions are formed when, for example, lead chloride is dissolved in an excess of hydrochloric acid.

Lead sulphate is also readily dissolved by certain acetates, citrates, and tartrates, especially ammonium salts, and by ammonium nitrate. This is probably due to the formation of complex ions in the case of the tartrates and citrates. In the case of the acetates it appears to be due to the exceptionally small degree of dissociation of lead acetate in solution. The explanation in the case of ammonium nitrate is still obscure.

The sulphate is decomposed and dissolved by solutions of the alkali hydroxides with the formation of PbO_2^{--}-anions, and is easily decomposed by alkali carbonate solutions. It should not be ignited at temperatures above a moderate red heat, as it is slowly decomposed at higher temperatures.

DETERMINATION OF COPPER

Procedure.—Transfer the filtrate from the lead sulphate to a 500 cc. graduated flask, washing out the beaker carefully. Measure off one-tenth of the solution, proceeding as described on page 46, but use a 50 cc. flask, and pour the solution into a plain beaker of about 80 cc. capacity and of tall

form. Add to the copper solution 1 gram of ammonium nitrate. The solution is then ready for the electrolytic deposition of the copper.

Meanwhile four platinum electrodes, two anodes and two cathodes, should be cleaned by gently scouring with sapolio and treatment with acid, and the two cathodes ignited gently, and cooled in a large desiccator. Weigh them carefully, and place one anode and one cathode in each solution. The connections should then be made with the binding posts (or other device for connection with the electric circuit), in such a way that the copper will be deposited upon the electrode with the larger surface, which is made the cathode. When the solution has been in the circuit for twenty hours or more, it may be tested for copper by adding enough water to the solution to raise the level of the liquid about $\frac{1}{4}$ inch on the electrode, stirring to insure uniformity, and observing after the lapse of about two hours whether there is a deposition of copper on the fresh surface of the electrode. If copper is deposited, more water must be added and the test repeated. When the deposition appears to be complete, proceed as follows: Make a siphon from small glass tubing and attach a short piece of clean rubber tubing to the longer arm. Fill the siphon with distilled water, pinch the rubber tube, and insert the siphon in the solution. Release the rubber tube over a beaker, and as the liquid siphons off pour distilled water into the upper beaker at about the same rate at which the liquid is drawn off, until an amount of water about equal to twice the original volume has been added. Then allow the siphon to empty the beaker, and quickly rinse off the electrodes by a *gentle* stream from the washbottle. All these washings and rinsings must be saved. Pour over the electrode and copper enough alcohol to remove adhering water, and dry only for a few moments at 105° C. Cool in a large desiccator and weigh.

Test the solution again for copper by adding an excess of ammonia to 5 cc., comparing this liquid with an equal quantity of distilled water, holding both over a white surface. If more

than a bare trace of copper is found, evaporate the solution to 100 cc., and place it in the circuit a second time, having meanwhile cleaned the electrode. The instructor should be consulted before final decision is made as to the necessity for this step. The test portion must be returned to the solution.

The increase in weight of the electrode represents directly the weight of copper from one-tenth of the solution. The percentage is therefore easily calculated.

Notes.—1. The removal of one-tenth of the solution for the determination of copper and zinc is necessitated by the difficulties which would be encountered if the precipitation of such large quantities of these metals as would come from 5 grams of the brass was attempted. The solution is therefore diluted to a definite volume (500 cc.), and exactly one-tenth (50 cc.) is measured off. The comments in Note 6, page 50, also apply here.

2. The presence of sufficient ammonium nitrate to react with the sulphuric acid in the solution lessens the tendency of the copper to deposit on the cathode in a spongy condition. The amount of the nitrate added should not greatly exceed 1 gram.

3. The electrodes should be freed from all greasy matter before using, and those portions upon which the metal will deposit should not be touched with the fingers after scouring.

4. Under the conditions named in the procedure, the copper may be deposited in satisfactory condition by a current from three cells of a "gravity battery," in series, or by the current which passes through three 10-candle incandescent lamps, in series, on a 110-volt circuit. This gives a current of about 0.1 ampere, and the deposition is usually complete after twenty to twenty-four hours. After the lapse of twelve to fifteen hours the current strength may, if desired, be increased to 0.2 ampere, which hastens the deposition of the remaining copper; but this should not be done until most of the copper has been precipitated. The time required for the deposition of the copper may be much shortened, and the conditions as to strength of current, acidity of solution, etc., may be altered,

if a rotating cathode is employed. This requires a special device, a description of which, with methods of procedure, is to be found in such works as E. F. Smith's *Electroanalysis*.

5. The solution which is electrolyzed contains Cu^{++}, H^+, NO_3^-, and SO_4^{--}-ions. Of these the Cu^{++} and H^+-ions move toward the cathode, and the others in the reverse direction. At the cathode the Cu^{++}-ions are discharged and deposited as Cu-atoms on the platinum; and so long as these ions are present in quantity in the solution, the H^+-ions (since the solution pressure of hydrogen is greater than that of copper, which means that the tendency to remain in the ionic condition is greater) are not converted into H-atoms or molecules to any considerable extent. On the other hand, after the deposition of the copper is nearly completed these H^+-ions are discharged at the cathode, and, as atoms, they react upon the nitric acid in the solution, reducing it, with the ultimate formation of ammonium compounds. The solution must not, therefore, be left too long in circuit, as its acidity may be even completely destroyed and, since zinc is deposited from feebly acid or alkaline solutions, the determination be worthless.

The reactions at the anode are similar in principle to those at the cathode. The NO_3^--ions or the SO_4^{--}-ions tend to approach the anode and be discharged. It appears probable, however, that all aqueous solutions contain some O^{--}-ions (from dissociated water), and, since the tendency of these to remain in the ionic condition is less than that of the NO_3^- or SO_4^{--}-ions, they are discharged, and oxygen gas escapes from the solution. (See Appendix.)

6. The electrodes should be washed as far as possible before the current is broken to prevent re-solution of the copper. If several solutions are connected in the same circuit, some provision must be made by which the breaking of the current shall be avoided when the electrodes in any one solution are removed. This can be easily accomplished by springing a piece of brass between the binding posts just before removing the electrodes.

7. The electrode is washed with alcohol to promote rapidity of drying. The copper should not remain in the hot closet

a moment longer than is necessary, as it tends to oxidize at the higher temperature.

8. A dark deposit on the anode indicates a precipitation of lead as peroxide. Such deposition is not infrequent, as the lead sulphate is not absolutely insoluble in the acid liquid from which it separates. This electrode may be weighed with the precipitate, then cleansed and again weighed, and the amount of lead calculated from the weight of the peroxide added to that found as sulphate in the corresponding solution.

The deposition of the lead on the anode as peroxide has been accounted for in two different ways. The first explanation assumes that the lead salt, such as lead nitrate, is hydrolyzed (although only to a very slight extent), and that the resulting $Pb(OH)_2$ is partially dissociated into $2H^+$-ions and a PbO_2^{--}-ion, the latter being discharged at the anode. The second assumption is to the effect that the NO_3^--ions, as they accumulate close to the surface of the anode, give rise to the formation of lead pernitrate, $Pb(NO_3)_4$, which hydrolyzes with the formation of PbO_2, which deposits upon the slightly roughened surface of the anode, and, when small in quantity, adheres sufficiently tenaciously to permit weighing. The precipitate usually retains some water, and must, if it amounts to more than a very few milligrams, be dried to constant weight at a temperature about 125° C.

To separate lead and copper by electrolysis it is necessary to maintain a moderate concentration of acid (usually nitric acid) in the solution. Under these conditions the H^+-ions are discharged at the cathode in preference to the Pb^{++}-ions, which would otherwise be precipitated with the copper.

DETERMINATION OF ZINC

Procedure.—Concentrate the solution from which the copper has been removed to 150 cc. Add to the cold solution dilute ammonia water cautiously until it barely smells of ammonia; then add *one drop* of a dilute solution of litmus, and drop in, with the aid of a dropper, dilute nitric acid (1 : 5) until the blue of the litmus just changes to red. It is important that this point should not be overstepped. Heat

the solution nearly to boiling and pour into it slowly a filtered solution of di-ammonium hydrogen phosphate[1] containing a weight of the phosphate about equal to twelve times that of the zinc to be precipitated. Keep the solution just below boiling for fifteen minutes, stirring frequently. If at the end of this time the amorphous precipitate has become crystalline, allow the solution to cool for about four hours (a longer time does no harm), and filter upon an asbestos filter in a porcelain Gooch crucible. The filter is prepared as described on page 24, and should be dried to constant weight at 105° C.

Wash the precipitate until free from sulphates with a warm 1 per cent. solution of the di-ammonium phosphate, and then five times with 50 per cent. alcohol. Then dry the crucible and precipitate for an hour at 105° C., and finally to constant weight. The filtrate should be made alkaline with ammonia and tested for zinc with a few drops of ammonium sulphide, allowing it to stand.

From the weight of the zinc ammonium phosphate $(ZnNH_4PO_4)$ calculate the weight of the zinc and the percentage of the latter in the brass, remembering that only one-tenth of the solution was used for this determination.

Notes.—1. The zinc ammonium phosphate is soluble both in acids and in ammonia. It is, therefore, necessary to precipitate the zinc in a nearly neutral solution, which is more accurately obtained by adding a drop of a litmus solution to the liquid than by the use of litmus paper.

2. The precipitate which first forms is amorphous, and may have a variable composition. On standing it becomes crystalline and then has the composition $Zn(NH_4)PO_4$. The precipitate then settles rapidly and is apt to occasion "bumping" if the solution is heated to boiling. Stirring promotes the crystallization.

3. In a carefully neutralized solution containing a con-

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[1] The ammonium phosphate which is commonly obtainable contains some mono-ammonium salt, and this is not satisfactory as a precipitant. It is advisable, therefore, to weigh out the amount of the salt required, dissolve it in a small volume of water, add a drop of phenolphthalein solution, and finally add dilute ammonium hydroxide solution cautiously until the solution just becomes pink, but do not add an excess.

siderable excess of the precipitant and also ammonium salts, the separation of the zinc is complete after standing four hours. The precipitate is washed first with a dilute solution of the phosphate to prevent a slight decomposition of the precipitate (as a result of hydrolysis) if hot water alone is used. The alcohol is added to the final wash-water to promote the subsequent drying.

4. If the ammonium sulphide produces a distinct precipitate, this should be collected on a small filter, dissolved in a few cubic centimeters of dilute nitric acid, and the zinc reprecipitated as phosphate.

5. If a platinum Gooch crucible is used, the precipitate may be ignited and weighed as $Zn_2P_2O_7$, or this may also be accomplished by cautiously heating the porcelain Gooch crucible within a nickel or iron crucible, used as a radiator. The heating must be very slow at first, as the escaping ammonia may reduce the precipitate if it is heated too quickly.

6. It has been found that some samples of asbestos are acted upon by the phosphate solution and lose weight. An error from this source may be avoided by determining the weight of the crucible and filter after weighing the precipitate. For this purpose the precipitate may be dissolved in dilute nitric acid, the asbestos washed thoroughly, and the crucible reweighed.

7. The ionic changes connected with the precipitation of the zinc as zinc ammonium phosphate are similar to those described for magnesium ammonium phosphate, except that the zinc precipitate is soluble in an excess of ammonium hydroxide, probably as a result of the formation of complex ions of the general character $Zn(NH_3)_4^{++}$.

8. The details of this method of precipitation of zinc are fully discussed in an article by Dakin, *Ztschr. Anal. Chem.*, **39**, (1900), 273.

DETERMINATION OF SILICA IN SILICATES

Of the natural and artificially prepared silicates a comparatively few are completely decomposed by acids, while a large number require to be disintegrated by fusion before complete solution can be accomplished. The minerals laumontite, wollastonite, tephroite, datolite, natrolite, olivine (chrysolite), and many basic slags are representatives of the first class of silicates; feldspar is a representative of the second group.

ANALYSIS OF A DECOMPOSABLE SILICATE

Grind the mineral to a fine powder. Weigh out two portions of 0.5 to 0.6 gram each into 300 cc. porcelain casseroles. Pour over them 15 cc. of water, and stir until the powder is evenly mixed with the water. Add 25 cc. of hydrochloride acid (1.12 sp. gr.) in small portions, and warm until the mineral is wholly disintegrated, as indicated by a flocculent residue and absence of grittiness under the stirring rod (if any remains undissolved). Evaporate the solution to dryness, stirring frequently until the residue is a dry powder, and heat the residue for at least one hour at a temperature 120–130° C. Moisten the residue with hydrochloric acid (1.2 sp. gr.), warm gently, making sure that the acid comes into contact with the whole of the residue, dilute to 200 cc., and bring to boiling. Filter off the silica without much delay, and wash five times with warm dilute hydrochloride acid (one part acid [1.12 sp. gr.] to three parts of water). Allow the filter to drain for a few moments, then place a clean beaker below the funnel and remove the filtrate and washings; evaporate them to dryness, dehydrate at 120–130° C. for two hours, and proceed as before, using a second filter to remove the silica after the second dehydration. Wash this filter with warm dilute hydrochloride acid, and wash *both* filters with hot water until free from hydrochloride acid, as shown by the silver chloride test. Transfer both filters to a platinum crucible and ignite as described on page 11; finally,

ignite for thirty minutes over the blast lamp, and then for periods of ten minutes, until the weight is constant.

When a constant weight has been obtained, pour into the crucible about 3 cc. of water, and then 3 cc. of hydrofluoric acid. *This must be done in a hood with a good draft, and great care must be taken that the acid does not come into contact with the hands, as it produces painful wounds.*

If the precipitate has dissolved in this quantity of acid, add two drops of concentrated sulphuric acid, and heat very slowly (always under the hood) until all the liquid has evaporated, finally igniting to redness. Cool in a desiccator, and weigh the residue. Deduct the weight of this residue from the previous apparent weight of silica, and from the difference calculate the percentage of silica present.

Notes.—1. If strong acid were poured directly upon the powdered silicate a partial separation of gelatinous silicic acid would occur, and this jelly-like mass would inclose particles of the unchanged mineral, protecting them from the action of the acid. The water is added to avoid this separation by distributing the particles and diluting the first portions of acid.

2. A flocculent residue will often remain after the decomposition of the mineral is effected. This is usually partially dehydrated silicic acid. Silicic acid is only completely held in solution by acids when it is in the fully hydrated condition, corresponding to the formula $Si(OH)_4$. This compound is very unstable and soon loses water, separating from solutions as the loss increases, until on protracted heating at temperatures about $100°$ C. it loses all its water and becomes nearly insoluble. The progress of the dehydration is indicated by the behavior of the solution, which as evaporation proceeds usually gelatinizes. On this account it is necessary to allow the solution to evaporate on a steam bath, or to stir it vigorously, to avoid loss by spattering.

3. It has been shown by Hillebrand that silicic acid cannot be completely dehydrated by a single evaporation and heating, nor by several such treatments, unless an intermediate filtration of the silica occurs. If, however, the silica is removed and the filtrates are again evaporated and the residue heated,

the amount of silica remaining in solution is usually negligible, although several evaporations and filtrations are required with some silicates to insure absolute accuracy. The underlying reasons for this are as yet obscure.

It is probable that heating at 120–130° C. is not absolutely necessary to dehydrate the silica; but it is recommended, as tending to leave the silica in a better condition for filtration than when the lower temperature of the water bath is used. This and many other points in the analysis of silicates are fully discussed by Dr. Hillebrand in his admirable monograph on "The Analysis of Silicate and Carbonate Rocks," Bulletin No. 305 of the United States Geological Survey.

4. To obtain pure silica the residue after evaporation must be thoroughly extracted by warming with hydrochloric acid, and the solution freely diluted to prevent, as far as possible, the inclosure of the residue in the particles of silica.

5. Aluminium and iron are likely to be thrown down as basic salts from hot, very dilute solutions of their chlorides, as a result of hydrolysis. If the silica were washed only with hot water, the solution of these chlorides remaining in the filter after the passage of the original filtrate would gradually become so dilute as to throw down basic salts within the pores of the filter, which would remain with the silica. To avoid this, an acid wash-water is used until the aluminium and iron are practically removed. The acid is then removed by water.

6. The silica undergoes no change during the ignition beyond the removal of all traces of water; but Hillebrand (*loc. cit.*) has shown that the silica holds moisture so tenaciously that prolonged ignition over the blast lamp is necessary to remove it entirely. This finely divided, ignited silica tends to absorb moisture, and should be weighed quickly.

7. Notwithstanding all precautions, the ignited precipitate of silica is rarely wholly pure. It is tested by volatilization of the silica as silicon fluoride after solution in hydrofluoric acid, and, if the analysis has been properly conducted, the residue, after treatment with the acids and ignition, should not exceed 1 mg.

The acid produces ulceration if brought into contact with the skin, and its fumes are excessively harmful if inhaled.

8. The impurities are probably weighed with the original precipitate in the form of oxides. The addition of the sulphuric acid displaces the hydrofluoric acid, and it may be assumed that the resulting sulphates (usually of iron or aluminium) are converted to oxides by the final ignition. It is obvious that unless the sulphuric and hydrofluoric acids used are known to leave no residue on evaporation, a quantity equal to that employed in the analysis must be evaporated and a correction applied for any residue found.

9. Some of the natural silicates which are decomposed by acids contain water of crystallization, or constitution, which is very readily given off. Such silicates cannot be preserved in desiccators after grinding without risk of loss of some of this water. They should be placed at once in stoppered weighing-tubes.

10. The solution of a silicate in an acid is the result of the combination of the H^+-ions of the acid and the silicate ions of the silicate to form the slightly ionized silicic acid. As a consequence, the concentration of the silicate ions in the solution is reduced nearly to zero, and more silicate dissolves to reëstablish the disturbed equilibrium. This process repeats itself until all of the silicate is brought into solution. The formula of the resulting silicic acid varies somewhat with the nature of the silicate and the conditions of solution, the more common acids being orthosilicic acid (H_4SiO_4) and metasilicic acid (H_2SiO_3). Both of these acids are unstable in solution and tend to lose water of composition, and the partially dehydrated acid separates, sometimes as a jelly and sometimes as a flocculent precipitate. Heating completes the conversion to the anhydride, SiO_2. The changes may be represented by the reactions:

$$SiO_3^{--} + 2H^+ = (H_2SiO_3) = H_2O + SiO_2.$$
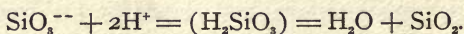
ANALYSIS OF A SILICATE UNDECOMPOSED BY ACIDS. (FELDSPAR)

Grind about 3 grams of the mineral in an agate mortar until no grittiness is to be detected when the mineral is placed between the teeth, or, better, until it will entirely pass through a sieve made of fine silk bolting cloth. The sieve may be made by placing a piece of the bolting cloth

over the top of a small beaker in which the ground mineral is placed, holding the cloth in place by means of a rubber band below the lip of the beaker. By inverting the beaker over clean paper and gently tapping it, the fine particles pass through the sieve, leaving the coarser particles within the beaker. These must be returned to the mortar and ground until they will *all* pass through the sieve.

Weigh out into platinum crucibles two portions of the ground feldspar of about 0.8 gram each. Weigh out on rough balances two portions of anhydrous sodium carbonate, each amounting to about six times the weight of the feldspar taken for analysis. Pour about three-fourths of the sodium carbonate into the crucible, place the latter on a piece of clean, glazed paper, and thoroughly mix the substance and the flux by carefully stirring for several minutes with a dry glass rod. The rod may be wiped off with a small fragment of filter paper, which may be placed in the crucible. Place the remaining fourth of the carbonate on the top of the mixture. Cover the crucible, heat it to dull redness for five minutes, and then gradually increase the heat to the full capacity of a Bunsen or Tirrill burner for twenty minutes, or until a quiet liquid fusion is obtained. Finally, heat the sides and cover strongly until any material which may have collected upon them is also brought to fusion.

Allow the crucible to cool, and remove the fused mass as directed on page 32. Disintegrate the fused mass by placing it in a previously prepared mixture of 100 cc. of water and 50 cc. of hydrochloric acid (sp. gr. 1.12) in a covered casserole. Clean the crucible and lid by means of a little hydrochloric acid, adding this acid to the main solution. When disintegration is complete, evaporate the solution to dryness and heat the residue to 120–130° C. for one hour. Proceed as described on page 67, repeating the evaporation and dehydration as there described.

Notes.—1. If the feldspar is in the massive or crystalline form, clean pieces should be selected and crushed in an iron

mortar to about half the size of a pea, and then transferred to a steel mortar, in which they are reduced to a coarse powder ready for the agate mortar. A wooden mallet should always be used to strike the pestle of the steel mortar, and the blows should not be sharp.

It is plain that the grinding must be continued until the whole of the portion of the mineral originally taken has been ground so that it will pass the bolting cloth, otherwise the sifted portion does not represent an average sample, the softer ingredients, if foreign matter is present, being first reduced to powder. For this reason it is best to start with about the quantity of the feldspar needed. Any coarse particles remaining would resist the action of the flux.

2. During the fusion the feldspar, which is strictly a silicate of aluminium and either sodium or potassium, but usually contains some iron, calcium, and magnesium, is decomposed by the alkaline flux, the sodium of the latter combining with the silicic acid of the silicate with the evolution of carbon dioxide, while about two-thirds of the aluminium forms sodium aluminate and the remainder is converted to a basic carbonate or the oxide. The calcium and magnesium, if present, are changed to carbonates or oxides, and, with the aluminium oxide, remain undissolved on treatment with water. The heat is applied gently to prevent a too violent reaction after fusion first takes place.

3. The silicic acid must be freed from its combination with a base (sodium, in this instance) before it can be dehydrated. The excess of hydrochloric acid accomplishes this liberation. By disintegrating the fused mass with a considerable volume of dilute acid the silicic acid is at first held in solution to a large extent, and on evaporation and re-solution of the bases the silica is left in a better condition for filtration and washing. Immediate treatment of the fused mass with strong acid is likely to cause the silicic acid to separate at once and to inclose alkali salts or alumina. The filtration should take place without delay, as the dehydrated silica appears to dissolve slowly in the hydrochloric acid.

4. A portion of the fused mass is usually projected upward by the escaping carbon dioxide during the fusion. The crucible must therefore be kept covered as much as possible and the lid carefully cleaned.

5. A gritty residue remaining after the disintegration of the fused mass by water indicates that the substance has been but imperfectly decomposed. Such a residue should be filtered, washed, dried, ignited, and again fused with the alkaline flux; or, if the quantity of material at hand will permit, it is better to reject the analysis, and to use increased care in grinding the mineral and in mixing it with the flux.

A large residue remaining after the volatilization of the silica also indicates imperfect decomposition of the feldspar by the fusion.

6. Quartz, and minerals containing very high percentages of silica, may require eight or ten parts by weight of the flux to insure a satisfactory decomposition.

7. The double evaporation and filtration spoken of in Note 3, page 68, are quite as essential here as in the case of a decomposable silicate, because of the relatively large amount of alkali salts (sodium chloride) present after evaporation. For the highest accuracy in the determination of silica, or of iron and alumina, it is also necessary to examine the precipitate produced by ammonium hydroxide for silica by fusion with acid potassium sulphate and solution of the fused mass in water. The insoluble silica is filtered, washed, and weighed, and the weight deducted from the apparent weight of the oxides.

PART III

VOLUMETRIC ANALYSIS

GENERAL DISCUSSION

IT has already been pointed out in Part I that the measurement of the volume of a solution required for a definite reaction takes the place in Volumetric Analysis of the weighing of the precipitated substance in Gravimetric Analysis.

It is plain that the analytical balance is equally requisite as a starting point for both systems; and it will be seen that the processes of volumetric analysis demand, beside an accurate balance, *standard solutions; i. e.,* solutions of accurately known value; *graduated instruments* in which to measure the volume of such solutions; and finally, some means which shall furnish an accurate indication of the point at which the desired reaction is completed. Those substances which furnish such information are called *indicators.* These will be discussed in connection with the different analyses.

The process whereby a standard solution is brought into reaction is called *titration,* and the point at which the reaction is exactly completed is called the *end-point.* The *indicator* should show the *end-point* of the *titration.*

The processes of Volumetric Analysis are easily classified, according to their character, into:

I. Saturation Methods; such, for example, as those of acidimetry and alkalimetry.

II. Oxidation Processes; as exemplified in the determination of ferrous iron by its oxidation with potassium bichromate.

III. Precipitation Methods; of which the titration for silver with potassium thiocyanate solution is an illustration.

From a somewhat different standpoint the methods may be subdivided into (a) *Direct Methods,* in which the sub-

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stance to be measured is directly determined by titration with a standard solution to an end-point; and (*b*) *Indirect Methods,* in which the substance itself is not measured, but a quantity of reagent is added which is known to be an excess with respect to a specific reaction, and the unused excess determined by titration. Examples of the latter class will be pointed out as they occur in the procedures.

Volumetric processes are, as a rule, more rapid and frequently more accurate than gravimetric processes having the same ends in view. The number of reactions capable of adaptation as volumetric methods is, however, somewhat limited.

STANDARD SOLUTIONS

The strength or value of a solution for a specific reaction is determined by a procedure called *Standardization,* in which the solution is brought into reaction with a definite weight of a substance of known purity. For example, a definite weight of pure sodium carbonate may be dissolved in water, and the volume of a solution of hydrochloric acid necessary to exactly neutralize the carbonate accurately determined. From these data the strength or value of the acid is known. It is then a *standard solution.*

Standard solutions may be made of a purely empirical strength, dictated solely by convenience of manipulation, or the concentration may be chosen with reference to a system which is applicable to all solutions, and based upon chemical equivalents. Such solutions usually bear some simple relation to a *Normal Solution* of the specific reagent; they are, for example, half-normal, deci-normal, or centi-normal solutions.

A *Normal Solution,* as defined by Mohr (*Titrirmethode,* p. 56), contains in 1 liter "one equivalent of the active reagent in grams." The "equivalent in grams" may be defined as "that quantity of the active reagent which contains, replaces, unites with, or in any way, directly or indirectly, brings into reaction 1 gram of hydrogen."

The application of this general statement to specific cases is pointed out below.

A liter of *normal acid solution* should contain that quantity of the reagent which represents 1 gram of hydrogen replaceable by a base. Accordingly, the normal solution of hydrochloric acid (HCl) should contain 36.45 grams of the gaseous compound, since that amount furnishes the requisite 1 gram of replaceable hydrogen. On the other hand, the normal solution of sulphuric acid (H_2SO_4) should contain only 49.03 grams, one-half of its molecular weight.

A *normal alkali solution* should contain sufficient alkali in a liter to replace 1 gram of hydrogen in an acid. This quantity is represented by the molecular weight in grams (40.05) of sodium hydrate (NaOH), while a sodium carbonate solution (Na_2CO_3) should contain but one-half the molecular weight in grams (*i. e.*, 53.05 grams) in a normal solution.

A normal solution of an *oxidizing agent* should contain one equivalent of available oxygen; that is, sufficient oxygen to unite with 1 gram of hydrogen to form water. The amount, for example, of potassium bichromate ($K_2Cr_2O_7$) which will furnish one equivalent of available oxygen is seen from the following considerations: The bichromate yields on reduction a salt of potassium corresponding to the oxide K_2O, and a salt of chromium corresponding to the oxide Cr_2O_3. The residual and available oxygen is represented by three atoms ($K_2Cr_2O_7 = K_2O + Cr_2O_3 + 3O$). Accordingly, 1 gram-molecule of the bichromate will furnish 6 equivalents of available oxygen, or enough to oxidize 6 grams of hydrogen to water, as seen from the equation, $6H_2 + 3O_2 = 6H_2O$. The definition, therefore, demands only one-sixth of the molecular weight (or 49.08 grams) for a normal solution.

A liter of a normal solution of a *reducing agent* must have the same reducing power as 1 gram of hydrogen. For example, a solution of stannous chloride must contain one-half of its molecular weight in grams per liter (94.95 grams), as indicated by the equations, $SnCl_2 + 2FeCl_3 = SnCl_4 +$

$2FeCl_2$ and $H_2 + 2FeCl_3 = 2HCl + 2FeCl_2$. One gram-molecule of the stannous chloride is plainly equivalent to 2 grams of hydrogen.

Normal solutions, since they rest upon a common foundation, have the advantage of uniformity. A liter of a normal solution of an acid will exactly neutralize a liter of a normal alkali solution, and a liter of a normal oxidizing solution exactly react with a liter of a normal reducing solution, and so on. It must be noted, however, that the same substance may sometimes have different equivalents when used under varying conditions; as, for example, potassium permanganate, two molecules of which yield three atoms of available oxygen (equivalent to six hydrogen atoms) in neutral solution, and five atoms of oxygen (equivalent to ten atoms of hydrogen) when used in acid solution. These facts must be considered when reference is made to a normal solution of that reagent, and the statement must specify the conditions of use.

Beside the advantage of uniformity, the use of normal solutions simplifies the calculations of the results of analyses. This is particularly true if, in connection with the normal solution, the weight of substance for analysis is chosen with reference to the molecular weight of the constituent to be determined. For illustrations of this, consult Part IV, page 142.

The preparation of an *exactly* normal, half-normal, or decinormal solution requires considerable time and care, as noted on page 96, and is usually carried out only when a large number of analyses are to be made, or when the analyst has some other specific purpose in view. It is, however, a comparatively easy matter to prepare standard solutions which differ but slightly from the normal or half-normal solutions, and these have the advantage of practical equality; that is, two approximately half-normal solutions are more convenient to work with than two which are widely different in strength. It is, however, true that whatever advantage pertains to the use of normal solutions as regards simplicity of calculations is, to a considerable extent, lost when using these approximate solutions.

GRADUATED INSTRUMENTS

A *burette* consists of a glass tube which is made as uniformly cylindrical as possible, and of such a bore that the divisions which are etched upon its surface shall correspond to actual contents as far as is practicable.

The tube is contracted at one extremity, and terminates in either a glass stopcock and delivery-tube (a Geissler burette), or in such a manner that a piece of rubber tubing may be firmly attached, connecting a delivery-tube of glass. The rubber tubing is closed by means of a pinch-cock or by a glass bead (Mohr burette).

The graduations are usually numbered in cubic centimeters, and the latter are subdivided into tenths.

A *pipette* may consist of a narrow tube, in the middle of which is blown a bulb of a capacity a little less than that which it is desired to measure by the pipette; or it may be a miniature burette, without the stopcock or rubber tip at the lower extremity. In either case, the flow of liquid is regulated by the pressure of the finger on the top, which governs the admission of the air.

Graduated or measuring flasks are similar to the ordinary flat-bottomed flasks, but are provided with long, narrow necks in order that slight variations in the position of the meniscus with respect to the graduation shall represent a minimum volume of liquid. The flasks must be of such a capacity that when filled with the specified volume the liquid rises well into the neck.

CALIBRATION OF INSTRUMENTS

If accuracy of results is to be attained, the correctness of all measuring instruments must be tested. None of the apparatus offered for sale can be implicitly relied upon except those more expensive instruments which are accompanied by a certificate from the *National Bureau of Standards* at Washington, the *Physikalische Reichsanstalt* in Berlin, or other equally authentic source.

The bore of burettes is subject to accidental variations, and since the graduations are applied without regard to such variations of bore, local errors are the result. The same statement applies to pipettes, while even the graduations upon flasks are often incorrect for the temperatures given. It is a general custom to purchase the flasks ungraduated and to graduate them for use under standard conditions selected for the laboratory in question.

The process of testing these instruments is called *Calibration*. It is usually accomplished by comparing the actual weight of water contained in the instrument with its apparent volume.

There is, unfortunately, no uniform standard of volume which has been adopted for general use in all laboratories. It has been variously proposed to consider the volume of 1000 grams of water at 4°, 15.5°, 16°, 17.5°, and even 20° C., as a liter for practical purposes, and to consider the cubic centimeter to be one-thousandth of that volume. The true liter is the volume of 1000 grams of water at 4° C.; but this is obviously a lower temperature than that found in our laboratories, and involves the constant use of corrections if taken as a laboratory standard. Mohr in his *Titrirmethode* adopts 17.5° C. as a practically useful temperature, and the volume of 1000 grams of water at 17.5° C. has been known as the "Mohr liter." Many laboratories use 15.5° C. (60° F.) as the working standard. It is plain that any temperature which is deemed most convenient might be chosen for a particular laboratory, but it cannot be too strongly emphasized that all measuring instruments, including flasks, pipettes, and burettes, should be calibrated at that temperature in order that the contents of each flask, pipette, etc., shall be comparable with that of every other instrument, thus permitting general interchange and substitution. For example, it is obvious that if it is desired to remove exactly 50 cc. from a solution which has been diluted to 500 cc. in a graduated flask, the 50 cc. flask or pipette used to remove the fractional portion must give a correct reading at the same temperature

as the 500 cc. flask. Similarly, a burette used for the titration of the 50 cc. of solution removed should be calibrated under the same conditions as the measuring flasks or pipettes employed with it.

The student should also bear constantly in mind that all volumetric operations to be exact should be conducted as nearly at a constant temperature as is practicable. The spot selected for such work should therefore be subject to a minimum of temperature variations, and should have as nearly the average temperature of the laboratory as is possible. In all work, whether of calibration, standardization, or analysis, the temperature of the liquids employed must be taken into account, and if the temperature of these liquids varies more than 3° or 4° from the standard temperature chosen for the laboratory, corrections must be applied for errors due to expansion or contraction, since volumes of a liquid measured at different times are comparable only under like conditions as to temperature. Data to be used for this purpose are given in the Appendix. Neglect of this correction is frequently an avoidable source of error and annoyance in otherwise excellent work. The temperature of all solutions at the time of standardization should be recorded to facilitate the application of temperature corrections, if such are necessary at any later time.

CALIBRATION OF BURETTES

Each student should calibrate at least one burette as follows:

Procedure.—Clean the burette thoroughly by pouring into it a warm solution of chromic acid in concentrated sulphuric acid. This solution can be prepared by adding to concentrated commercial sulphuric acid a few crystals of potassium bichromate and a little water. Warm the mixture gently and pour off the solution. It is convenient to have such a solution at hand, as burettes frequently need cleaning. The rubber tip should be removed from a burette before the cleansing agent is added.

Stopper the burette and bring the acid in contact with its entire length by shaking. Pour the acid back into its receptacle and wash out the burette thoroughly with water. Unless the water runs from the burette without leaving drops upon the sides the process must be repeated. When clean, fill the burette with distilled water which has been standing for at least a half hour near the spot at which the burette is to be used. Note the temperature of this water. Allow the water to run out through the stopcock or rubber tip until convinced that no air bubbles are inclosed. Fill the burette to the zero mark and draw off the liquid until the meniscus is just below the zero mark. To take the exact reading, wrap around the burette a piece of colored paper with its straight, smooth edges evenly together (color turned inside), held two small divisions below the meniscus. Move the eye so that the edge of the paper at the back of the burette is just hidden by that in front, and note the position of the lowest point of the meniscus of the water. Estimate the tenths of the small divisions, corresponding to hundredths of a cubic centimeter, and record the reading in the notebook.

Weigh a 50 cc. flat-bottomed flask (preferably a light weight flask), which must be dry on the outside, to the nearest centigram. Record the weight in the notebook. Place the flask under the burette and draw out into it about 10 cc. of water, removing any drop on the tip by touching it against the inside of the neck of the flask. Do not attempt to stop exactly at the 10 cc. mark, but do not vary more than 0.1 cc. from it. Note the time, and at the expiration of three minutes (or longer) take the reading upon the burette accurately, and record it in the notebook. Meanwhile weigh the flask and water to centigrams and record its weight. Draw off the liquid from 10 cc. to about 20 cc. into the same flask without emptying it; weigh, and at the expiration of three minutes take the reading, and so on throughout the length of the burette. When it is completed, refill the burette and check the first calibration.

The differences in readings represent the apparent volumes, the differences in weights the true volumes. For example, if an apparent volume of 10.05 was found to weigh 10.03 grams, it may be assumed with sufficient accuracy that the error in that 10 cc. amounts to 0.02 cc., or 0.002 for each cubic centimeter. The records may conveniently be made in the notebook under these headings:

Burette readings	Differences	Observed weights	Differences	Calculated corrections

In the calculation of corrections the temperature of the water must be taken into account, if this varies more than 4° C. from the laboratory standard temperature, consulting the table of densities of water in the Appendix.

From the final data plot the corrections to be applied so that they may be easily read for each cubic centimeter throughout the burette. The total correction at each 10 cc. may also be written on the burette with a diamond for permanence of record.

> *Notes.*— 1. The inner surface of the burette must be absolutely clean if the liquid is to run off freely. Chromic acid in sulphuric acid is usually found to be the best cleansing agent, but the mixture must be warm and concentrated.
>
> 2. It is always necessary to insure the absence of air bubbles in the tips by running the liquid rapidly through them. These bubbles may otherwise escape during calibration or titration and vitiate results.
>
> 3. To obtain an accurate reading the eye must be on a level with the meniscus. This may be attained by the use of a paper or by using a float. The latter is useful provided it moves freely in the burette, but care must be taken that such is the case, otherwise a float is worse than useless.
>
> 4. The eye soon becomes accustomed to estimating the tenths of the divisions. If the paper is held as directed, two divisions below the meniscus, one whole division is visible to correct the judgment. It is not well to attempt to bring the meniscus exactly to a division mark on the burette. Such

readings are usually less accurate than those in which the tenths of a division are estimated.

5. It is obvious that it would be useless to weigh the water with an accuracy greater than that of the readings taken on the burette. The latter cannot exceed 0.01 cc. in accuracy, which corresponds to 0.01 gram.

The student should clearly understand that *all other weighings*, except those for calibration, should be made accurately to 0.0001 gram, unless special directions are given to the contrary.

Corrections for temperature variations of less than 4° C. are negligible, as they amount to less than 0.01 gram for each 10 grams of water withdrawn.

6. A small quantity of liquid at first adheres to the side of even a clean burette. This slowly unites with the main body of liquid, but requires an appreciable time. Three minutes is a sufficient interval, but not too long, and should be adopted in every instance throughout the whole volumetric practice before final readings are recorded.

7. Should the error discovered in any interval of 10 cc. on the burette exceed 0.10 cc., it is advisable to weigh smaller portions (even 1 cc.) to locate the position of the variation of bore in the tube rather than to distribute the correction uniformly over the corresponding 10 cc. The latter is the usual course for small corrections, and it is convenient to calculate the correction corresponding to each cubic centimeter and to record it in the form of a table or calibration card, or to plot a curve representing the values.

8. Burettes may also be calibrated by drawing off the liquid in successive portions through a 5 cc. pipette which has been accurately calibrated, as a substitute for weighing. If many burettes are to be examined this is a more rapid method.

9. Pipettes are calibrated in the same general way as burettes. They must be cleaned and are then filled with water, and the latter is drawn off and weighed. A definite interval must be allowed for draining, and a definite practice adopted with respect to the removal of the liquid which collects at the end of the tube, if the pipette is designed to deliver a specific volume when emptied. This liquid may be removed at the end of a definite interval either by touching

the side of the vessel or by gently blowing out the last drops. Either practice must be uniformly adhered to.

Procedure.—Clean the flask and dry it carefully outside and inside. Tare it accurately, and place on the opposite balance-pan the number of grams corresponding to the volume desired; pour water into the flask until the weight of the latter counterbalances the weight on the pan, removing any excess of water with the aid of filter paper. Take the flask from the balance, stopper it, place it in a bath at the desired temperature, usually 15.5° or 17.5°C., and after an hour mark on the neck with a diamond the location of the lowest point of the meniscus.

Notes.—1. The allowable error in counterbalancing the water and weights varies with the volume of the flask. It should not exceed one ten-thousandth of the weight of water.

2. Other methods are employed which involve the use of calibrated apparatus from which the desired volume of water may be run into the dry flask and the graduation marked directly upon it. For a description of one of these which is most convenient when many flasks are to be calibrated, the student is referred to the *Am. Chem. J.,* 16, 479.

3. Flasks may be graduated either for "contents" or for "delivery." In the former case they contain the specified volume when filled to the graduation; in the latter case the flask will deliver the specified volume if allowed to drain for a definite time. By placing two marks upon the flask it may be graduated for both contents and delivery.

To calibrate a flask for delivery it should be filled with water, then emptied and allowed to drain for a definite interval (three minutes). It is then tared, the requisite weights are placed upon the balance-pan, and water added to counterbalance these. It is then placed in a bath at the required temperature, and marked after an hour.

Flasks thus calibrated will deliver a definite volume of a solution without being washed out. It is, however, a more general custom to graduate flasks for contents.

GENERAL DIRECTIONS

It is essential to the success of analyses that uniformity of practice shall prevail throughout all volumetric work with respect to those matters which can influence the accuracy of measurement of liquids. Whatever conditions are imposed, for example, during the calibration of a burette, pipette, or flask (notably the time allowed for draining), must also prevail *whenever* the flask or burette is used.

The student should be constantly watchful to insure parallel conditions during both standardization and analysis with respect to the final volume of liquid in which a titration takes place. The standard of the solution is only accurate under the conditions which prevailed when it was determined.

It is plain that the standard solutions must be scrupulously protected from concentration or dilution, after their value has been established. Accordingly, great care must be taken to thoroughly rinse out all burettes, flasks, etc., with the solutions which they are to contain, in order to remove all traces of water or other liquid which could act as a diluent. It is best to wash out a burette at least three times with small portions of a solution, allowing them to run out through the tip, before assuming that it is in a condition to be filled and used. It is, of course, possible to dry the measuring instruments in a hot closet, but this is tedious and unnecessary.

To the same end, all solutions should be kept stoppered and away from direct sunlight or heat. The bottles should be shaken before use to collect any liquid which may have distilled from the solution and condensed on the sides.

The student is again reminded that variations in temperature of volumetric solutions must be carefully noted, and care should always be taken that no source of heat is sufficiently near the solutions to raise the temperature during use.

Much time may be saved by estimating the approximate volume of a standard solution which will be required for a titration (if the data are obtainable) before beginning the

operation. It is then possible to run in rapidly approximately the required amount, after which it is only necessary to determine the end-point with accuracy. In such cases, however, the knowledge of the amount probably to be required should never be allowed to influence the judgment regarding the actual end-point.

I. SATURATION METHODS

ALKALIMETRY AND ACIDIMETRY

GENERAL DISCUSSION

Standard solutions of acid and alkali are required for these processes, together with such indicators as will accurately designate the point of saturation.

Standard Acid Solutions may properly be prepared from either hydrochloric, sulphuric, or oxalic acids. Hydrochloric acid has the advantage of forming soluble compounds with the alkaline earths, but its solutions cannot be boiled without danger of loss of strength; sulphuric acid solutions may be boiled without loss, but the acid forms insoluble sulphates of three of the alkaline earths; oxalic acid can be accurately weighed for the preparation of solutions, and its solutions may be boiled without loss; but it also forms insoluble oxalates with three of the alkaline earths, and cannot be used with certain of the indicators.

Standard Alkali Solutions may be prepared from sodium or potassium hydroxide, sodium carbonate, barium hydroxide, or ammonia. Of sodium and potassium hydroxide, it may be said that they can be used with all indicators, and their solutions may be boiled, but they absorb carbon dioxide readily and attack the glass of bottles; sodium carbonate may be weighed directly if its purity is assured, but the presence of the carbonic acid of the carbonate is a disadvantage with many indicators; barium hydroxide solutions may be prepared which are entirely free from carbon dioxide, and such solutions immediately show by precipitation any contamination from absorption, but the hydroxide is not freely soluble in water; ammonia does not absorb carbon dioxide as readily as the caustic alkalies, but its solutions cannot be boiled nor can they be used with all indicators. The choice of a solution must depend upon the nature of the work in hand.

Half-normal ($\frac{N}{2}$) or deci-normal ($\frac{N}{10}$) solutions are employed in most analyses (except in the case of the less soluble barium hydroxide). Solutions of the latter strength are convenient when small percentages of acid or alkali are to be determined.

INDICATORS

The substances used as indicators in alkalimetric or acidimetric processes comprise a considerable number of organic bodies, often of very complicated structure, the common characteristic of which is the property of imparting a different color to solutions according to their acidity or alkalinity. The change of color must be produced by even a slight excess of either H^+ or OH^--ions, as, for example, is the case with litmus, which is a characteristic indicator.

Of the substances used as indicators a few are weak bases, a few are pronounced (but not strong) acids, while the majority are weak acids. Their basic or acidic properties determine their efficiency in a given case, for they are not all equally useful. Some of those most commonly employed are given in the table below in the order of their sensitiveness toward an alkali; that is, their efficiency in detecting the presence of any free OH^--ions in the solution. The figures given represent the amount of deci-normal sodium hydroxide solution required to produce an alkaline reaction when run into 10 cc. of deci-normal sulphuric acid solution diluted with 50 cc. of distilled water to which five drops of indicator solution have been added.[1]

Indicator.	$\frac{N}{10}$ H$_2$SO$_4$	$\frac{N}{10}$ NaOH	Color in acid solution.	Color in alkaline solution.
	cc.	cc.		
Methyl orange	10	9.90	Red	Yellow
Lacmoid	10	10.00	Red	Blue
Litmus	10	10.00	Red	Blue
Rosalic acid	10	10.07	Yellow	Pink
Phenolphthaleïn	10	10.10	Colorless	Pink

[1] Glaser, *Indikatoren der Acidimetrie und Alkalimetrie.* Wiesbaden, 1901.

Phenolphthalëin is the most sensitive of these indicators toward acids, as methyl orange is toward alkalies, the others occupying an intermediate position. When a strong acid, such as hydrochloric, sulphuric or nitric acid, is titrated against a strong base, such as sodium hydroxide, potassium hydroxide, or barium hydroxide, any of these indicators may be used; but it is evident from the table that in order to secure accurate results the same indicator should be used for both standardization and analysis. When, however, the substance to be titrated is either a weak base, as ammonium hydroxide, or a weak acid, such as boric, acetic, citric, or other organic acids, a careful selection of an indicator must be made for reasons given below. Certain acids, such as oxalic acid or tartaric acid, occupy an intermediate position as to strength; and, again, certain unstable or volatile acids, as carbonic acid or hydrogen sulphide, must be taken into account in the selection of an indicator for use in a particular titration.

In the following discussion of the principles underlying the behavior of the indicators as a class, methyl orange and phenolphthalëin are taken as types. It has already been pointed out that the indicators are bodies of complicated and not always of well-understood structure, and the exact nature of the changes which they undergo is not always known. In the case of the two indicators named, however, this has been carefully studied by Stieglitz (*J. Am. Chem. Soc.*, **25**, 1112) and others, and it appears that the changes involved are of two sorts: First, a rearrangement of the atoms within the molecule, such as often occurs in organic compounds; and, second, ionic changes. The intermolecular changes cannot appropriately be discussed here, as they involve a somewhat detailed knowledge of the classification and general behavior of organic compounds; they will, therefore, be merely alluded to, and only the ionic changes followed.

Methyl orange in aqueous solution behaves as a very weak base. The yellow color of such solutions is probably produced by the undissociated base. If, now, an acid, as HCl, is added to such a solution, the base of the indicator reacts

with the acid as in any neutralization reaction, with the consequent formation of a salt, as indicated, for example, by the reaction (M.o.)$^+$, OH$^-$ + H$^+$, Cl$^- \rightleftharpoons$ (M.o.)$^+$, Cl$^-$ + H$_2$O. This salt would naturally ionize into (M.o.)$^+$, using this abbreviation for the positive complex, and Cl$^-$; but simultaneously with its formation there appears to be an internal rearrangement of the atoms which results in the production of a red salt, with a cation which may be designated as (M'.o'.)$^+$, and this imparts a characteristic color to the solution. As these changes occur in the presence of even a small excess of acid (that is, of H$^+$-ions), it serves as the desired index of their presence in the solution. If, now, the process is reversed and an alkali, as NaOH, is added to this reddened solution, the reverse series of changes also takes place. As soon as the free acid present is neutralized, the slightest excess of sodium hydroxide, acting as a strong base, sets free the weak base of the indicator, and at the moment of its formation it reverts, because of the rearrangement of the atoms, to the yellow form, OH$^-$ + (M'.o') $\rightarrow$ (M'.o'.OH) $\rightarrow$ (M.o.OH).

Phenolphthalëin, on the other hand, is a very weak acid, which is colorless in aqueous solutions or in the presence of free acid. When, however, an alkali is added to such a solution in excess, a salt is formed according to the reaction, H$^+$,(Ph)$^-$ + Na$^+$,OH$^- \rightleftharpoons$ Na$^+$,(Ph)$^-$ + (H$_2$O). But in this case, also, a rearrangement of the atoms occurs, and a pink salt with a new ion, (Ph')$^-$, is formed, which imparts a pink color to the solution. The addition of the slightest excess of an acid to this solution, on the other hand, occasions the setting free of the undissociated acid of the indicator and its reversion to the colorless form, H$^+$ + Ph'$^- \rightarrow$ (HPh') $\rightarrow$ (HPh).

To understand why methyl orange is the most sensitive of the common indicators toward an excess of alkali, it should be remembered that since it is a very weak base, and therefore very slightly dissociated, this free base should form immediately when even the slightest excess of OH$^-$-ions is present in a solution, and the change from red to yellow should be prompt and sharp. On the other hand, it should be an

inefficient indicator toward weak acids, because the salt formed from this weak base is hydrolyzed, as is shown by the following equation, and this obscures the true end-point: $(M'.o')^+$, $C_2H_3O_2^- + H^+,OH^- = [(M'.o')OH] + H^+,C_2H_3O_2^-$. In the case of strong acids this hydrolytic action is so far diminished by the presence of the H^+-ions from these acids that the indicator is satisfactory; but with weak acids the hydrolysis of the salts proceeds so far that the end-point is uncertain, and methyl orange cannot be used with such acids. With the very weak acids, such as carbonic acid or hydrogen sulphide, the salts are almost completely hydrolyzed, and the indicator is scarcely affected by these acids. This explains its usefulness, as referred to later, for the titration of strong acids in the presence of carbonates or sulphides in solution.

Phenolphthalëin, on the other hand, should be, as it is, the best of the common indicators for use with weak acids. Since it is itself a weak acid, it is very little dissociated, and accordingly its undissociated, colorless molecules are promptly produced as soon as there is any free acid (that is, free H^+-ions) in the solution. But in the presence of alkalies, since it is a weak acid, it forms salts which are easily hydrolyzed, and under these conditions there is a partial reversion to the colorless molecules, which renders the change of color less sharp in the presence of an excess of alkali than in the presence of an acid. The indicator can, however, be successfully used with strong bases, because the excess of OH^--ions from these bases diminishes the hydrolytic action; but ammonium hydroxide forms salts which are so largely hydrolyzed that this weaker alkali cannot be accurately measured when phenolphthalëin is used.

This indicator is affected by carbonic acid, which must be removed by boiling the solution before titration. It is the indicator most generally employed for the titration of organic acids.

Glaser (*loc. cit.*) points out that secondary changes may occur which cause some variations of the sensitiveness of a given indicator if the dilution and temperature of the solutions

vary widely. It is important, therefore, to take pains to use approximately the same volume of solution when standardizing that is likely to be employed in analysis; and when it is necessary, as is often the case, to titrate the solution at boiling temperature, the standardization should take place under the same conditions. It is also obvious that since some acid or alkali is required to react with the indicator itself, the amount used should be uniform and not excessive. Usually a few drops of solution will suffice.

A methyl orange solution for use as an indicator is commonly made by dissolving 0.05–0.1 gram of the compound (also known as Orange III) in a few cubic centimeters of alcohol and diluting with water to 100 cc. The grade of material which is prepared for indicator purposes should be secured. It can be successfully used for the titration of hydrochloric, nitric, sulphuric, phosphoric, and sulphurous acids, and is particularly useful in the determination of bases, such as sodium, potassium, barium, calcium, and ammonium hydroxides, and even many of the weak organic bases. It can also be used for the determination, by titration with a standard solution of a strong acid, of the salts of weak acids, such as carbonates, sulphides, arsenites, borates, and silicates, because the weak acids which are liberated do not affect the indicator, and the reddening of the solution does not take place until an excess of the strong acid is added. It should be used in cold, not too dilute solutions. Its sensitiveness is lessened in the presence of considerable quantities of the salts of the alkalies.

Phenolphthalëin solution is prepared by dissolving 1 gram of the pure compound in 100 cc. of 96 per cent. alcohol.

This indicator is particularly valuable in the determination of weak acids, especially organic acids. It cannot be used with weak bases, even ammonia. It is affected by carbonic acid, which must, therefore, be removed by heating when other acids are to be measured. It can be used in hot solutions. Some care is necessary to keep the volume of the solutions to be titrated approximately uniform in standardization and in analysis, and this volume should not in general

exceed 125–150 cc. for the best results, since the compounds formed by the indicator undergo changes in very dilute solution which lessen its sensitiveness.

The preparation of a solution of litmus which is suitable for use as an indicator involves the separation from the commercial litmus of azolithmine, the true coloring principle. The litmus as supplied to the market is mixed with calcium carbonate or sulphate and compressed into lumps. These are powdered and treated two or three times with alcohol,[1] which dissolves out certain constituents which cause a troublesome intermediate color if not removed. The alcohol is decanted and drained off, after which the litmus is extracted with hot water until exhausted. The solution is allowed to settle for some time, the clear liquid siphoned off, concentrated to one-third its volume, and acetic acid added in slight excess. It is then concentrated to a sirup, and a large excess of 90 per cent. alcohol added to it. This precipitates the blue coloring matter, which is filtered off, washed with alcohol, and finally dissolved in a small volume of water and diluted until about three drops of the solution added to 50 cc. of water produce a distinct color. This solution must be kept in an unstoppered bottle, and may well be protected from dust by a loose plug of absorbent cotton. If kept in a closed bottle it soon undergoes a reduction and loses its color, which, however, is often restored by exposure to the air.

Litmus can be employed successfully with the strong acids and bases, and also with ammonium hydroxide, although the salts of the latter influence the indicator unfavorably if present in considerable concentration. It may be employed with some of the stronger organic acids, but the use of phenolphthalëin is to be preferred.

PREPARATION OF HALF–NORMAL SOLUTIONS OF HYDRO–CHLORIC ACID AND SODIUM HYDROXIDE

Procedure.—Calculate the number of cubic centimeters of aqueous hydrochloric acid (sp. gr. 1.12 or 1.2) required to

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[1] Glaser, *loc. cit.*, p. 79. Various modifications of this procedure are also described.

furnish 36.45 grams of the gaseous compound. (For this purpose consult the Appendix.) Measure out a volume of acid about 10 per cent. in excess of the calculated quantity into a clean 2-liter bottle, and dilute with distilled water to an approximate volume of 2000 cc. Shake the solution thoroughly for a full minute to insure uniformity. Be sure that the bottle is not too full to permit of a thorough mixing, since lack of care at this point will be the cause of much wasted time.

Weigh out upon rough balances about 46 grams of sodium hydroxide. Dissolve the hydroxide in water and dilute to 2000 cc. Shake this solution also for a minute.

Select two clean burettes and fill them with the solutions, after rinsing them out *three times* with 10 cc. of the solution each time, which should be allowed to run out through the tip to insure the displacement of all water from that part of the burette. Note the temperature of the solutions, and when the burettes are ready for use and all air bubbles displaced from the tip, note the exact position of the liquid in each, and record the readings in the notebook. Run out from the burette about 40 cc. of the acid into a beaker, and add two drops of a solution of methyl orange; dilute the acid to about 80 cc., and run out alkali solution from the other burette until the pink has given place to a yellow. Wash down the sides of the beaker with a little distilled water if the solution has spattered upon them, return the beaker to the acid burette, and add acid to restore the pink; continue these alternations until the point is accurately fixed at which a single small drop of either solution serves to produce a distinct change of color. Select as the end-point the appearance of the faintest pink tinge which can be recognized, or the disappearance of this tinge, leaving a pure yellow; but always titrate to the same point. If the titration has occupied more than the three minutes required for draining the sides of the burette, the readings of the burettes may be immediately taken and recorded in the notebook.

Refill the burettes and repeat the titration. Correct the

burette readings as indicated by the burette calibrations, and for temperature if necessary, and obtain the ratio of the sodium hydroxide solution to that of hydrochloric acid by dividing the number of cubic centimeters of acid used by the number of cubic centimeters of alkali required for neutralization. The check results should not vary by more than two parts in one thousand.

When this ratio has been satisfactorily established the hydrochloric acid solution is standardized as follows: Place in a platinum crucible about 6 grams of the purest sodium bicarbonate obtainable, and put the platinum crucible inside of a larger nickel, iron, or porcelain crucible, supporting it upon a triangle of iron or copper wire in such a way that there is an air space of about ⅜ inch between them. Insert a thermometer reading to 300° C. in the bicarbonate, supporting it from a clamp so that the bulb does not rest on the bottom of the crucible. Heat the outside crucible, using a rather small flame, and raise the temperature of the bicarbonate fairly rapidly to 270° C. Then regulate the heat in such a way that the temperature rises *slowly* to 300° C. in the course of a half hour. The bicarbonate should be frequently stirred with a clean, dry, glass rod, and after stirring should be heaped up around the bulb of the thermometer in such a way as to cover it. This will require attention during most of the heating, as the temperature should not be permitted to rise above 310° C. for any length of time. At the end of the half hour remove the thermometer and transfer the platinum crucible, which now contains sodium carbonate, to a desiccator. When it is cold transfer it to a stoppered weighing-tube or weighing-bottle and weigh out into 400 cc. beakers two portions of about 1 gram each, noting the exact weights (to 0.0001 gram) in the notebook. Pour over the carbonate about 80 cc. of water, stir until solution is complete, and add two drops of methyl orange solution. Fill the burettes with the standard acid and alkali solutions, noting the initial readings of the burettes and temperature of the solutions. Run in acid from the burette, stirring and avoiding loss by

effervescence, until the solution has become pink. Wash down the sides of the beaker with a *little* water from a wash-bottle, and then run in alkali from the other burette until the pink is replaced by yellow; then finish the titration as described above. Note the readings on the burette after the proper interval, and record them in the notebook. From the data then recorded it is possible to determine the volume of hydrochloric acid neutralized by the pure sodium carbonate, and hence the relation of the hydrochloric acid solution to a normal solution. The standardization must be repeated until these values agree within at most two parts in one thousand.

From the ratio just obtained the degree of dilution required to prepare an exactly half-normal solution may be easily calculated. (For example, a solution which was found to have a value 0.5215 N should be diluted according to the proportion $0.5215 : 0.5 = x : 1000$; that is, each 1000 cc. of that solution should be diluted to 1043 cc.) Measure off 1500 cc. accurately in graduated flasks, observing precautions mentioned on page 46, and add the requisite volume of water from a burette. From the known ratio of the two solutions and the known value of the acid, calculate the requisite dilution for the alkali solution, and add the necessary volume of water to it also. Determine the ratio between these new solutions after shaking thoroughly, and restandardize the acid against sodium carbonate. The values thus found should not differ from the calculated values for half-normal solutions by more than one to two parts per thousand in either case. If a greater variation is found, the dilution and standardization must be repeated before the solutions are ready for use.

Notes.—1. The original solutions are prepared of greater strength than that finally desired, as they are more readily diluted than strengthened. Commercial sodium hydroxide is usually impure and always contains more or less carbonate; a further allowance is therefore made for this factor by placing the weight taken at 46 grams for the 2 liters. If the

hydroxide is known to be pure, a lesser amount (say 42 grams) will suffice.

2. Too much care cannot be taken to insure perfect uniformity of solutions before standardization, and thoroughness in this respect will, as stated, often avoid much waste of time. A solution once thoroughly mixed remains uniform.

3. The liquid is diluted to 100 cc. during standardization to make the volume approximately equal to that which will prevail during analysis. Compare remarks on page 92.

4. The end-point should be chosen exactly at the point of change; any darker tint is unsatisfactory, since it is impossible to carry shades of color in the memory and to duplicate them from day to day.

5. A variation of two parts in one thousand in the values obtained by an inexperienced analyst is not excessive, but the idea must be carefully avoided that this is a standard for accurate work to be generally applied. In many cases, after experience is gained, the allowable error is less than this proportion; in a few cases a larger variation is permissible.

6. The selection of the best substance to be used as a standard for acid solutions has been the subject of much controversy. In many works, and in previous editions of this manual, calcium carbonate has been recommended, and also sodium carbonate when directly purchased for this purpose. The work of Lunge (*Ztschr. angew. Chem.*, **1904,** 231), Ferguson (*J. S. C. I.*, **24,** 784), and others, seems to indicate that the best standard is sodium carbonate prepared from sodium bicarbonate by heating the latter at temperatures between 270° and 300° C. The bicarbonate is easily prepared in a pure state, and at the temperatures named the decomposition takes place according to the equation, $2HNaCO_3 = Na_2CO_3 + H_2O + CO_2$, and without loss of any CO_2 from the sodium carbonate, such as may occur at higher temperatures.

7. Instead of standardizing the acid solution as described, it is equally practicable to standardize the alkali solution against purified oxalic acid $(C_2H_2O_4.2H_2O)$, potassium acid oxalate $(KHC_2O_4.H_2O)$, potassium tetroxalate $(KHC_2O_4.C_2H_2O_4.2H_2O)$, or potassium acid tartrate $(KHC_4H_4O_6)$, with

the use of a suitable indicator. The oxalic acid and the oxalates should be specially prepared to insure purity, the main difficulty lying in the preservation of the water of crystallization.

It should be noted that the acid oxalate and the acid tartrate each contain one hydrogen atom replaceable by a base, while the tetroxalate contains three such atoms and the oxalic acid two. Each of the two salts first named behave as monobasic acids, and the tetroxalate as a tribasic acid.

8. It is also possible to standardize a hydrochloric acid solution by precipitating the chloride ions as silver chloride and weighing the precipitate, as prescribed under the analysis of sodium chloride. Sulphuric acid solutions may be standardized by precipitation of the sulphate ions as barium sulphate and weighing the ignited precipitate; but the results are not above criticism on account of the difficulty in obtaining large precipitates of barium sulphate which are uncontaminated by inclosures or are not reduced on ignition.

9. An inspection of the ionic equation, $Na^+, OH^- + H^+, Cl^- = Na^+, Cl^- + (H_2O)$, which is typical of neutralization reactions, shows that the ionic change consists in the union of H^+ and OH^--ions to form water, and it is also evident that the reaction can only be considered to be exactly completed if we assume that the water is undissociated. In point of fact, water is slightly dissociated, and the reaction is not, therefore, completed in an exact sense, for there are some H^+ and OH^--ions in the solution. Whether or not these are of practical significance in a particular instance will depend upon the strength of the acid or base used and the indicator chosen; that is, upon the effects of hydrolysis of the salts which are formed. These matters are discussed on pages 90 and 91.

DETERMINATION OF THE TOTAL ALKALINE STRENGTH OF SODA ASH

Procedure.—Weigh out on the laboratory balances two portions of soda ash of about 5 grams each. Place them on small watch-glasses and dry them at 110° C., until the weight is constant within 0.005 gram, weighing at intervals of thirty minutes and cooling in a desiccator. Finally, weigh accurately,

and transfer the soda ash to a 500 cc. lipped beaker; weigh the watch-glasses, and take the difference as the weight of the sample for analysis. Dissolve the ash in 75 cc. of water, warming gently, and filter off the insoluble residue; wash the filter until the washings are freed from carbonate, cool the filtrate approximately to the standard temperature of the laboratory, and transfer it to a 250 cc. measuring flask, washing out the beaker thoroughly. Add distilled water until the lowest point of the meniscus is level with the graduation on the neck of the flask, and remove any drops of water that may be on the neck above the graduation by means of a strip of filter paper; make the solution thoroughly uniform by pouring it out into a dry beaker and back into the flask several times.

Measure off 50 cc. of this solution in a measuring flask, but rinse out the smaller flask with at least two small portions of the soda ash solution to displace any water. Finally, fill the flask to the mark with the solution, and remove any drops on the neck above the graduation. Empty it into a beaker and wash out the small flask, unless it is graduated to *deliver* 50 cc., using as little water as practicable. (Compare Note 3, page 84, and the remarks on page 6.) Dilute the solution in the beaker to 100 cc., add two drops of methyl orange solution, and titrate for the alkali with the half-normal acid, using the half-normal alkali to complete the titration, as described under the preparation of solutions. From the volumes of acid and alkali employed, corrected for burette errors and temperature changes, and the data derived from the standardization, calculate the percentage of alkali present, assuming it all to be present as sodium carbonate.

It is advisable to measure out a second portion of 50 cc. from the main solution in each case to confirm the original titration.

Notes.—1. Soda ash is crude sodium carbonate. If made by the ammonia process it may contain also sodium chloride, sulphate, and hydrate; when made by the Le Blanc process it may contain sodium sulphide, silicate, and aluminate, and

other impurities. Some of these, notably the hydrate, combine with acids and contribute to the total alkaline strength, but it is customary to calculate this strength in terms of sodium carbonate; *i. e.*, as though no other alkali were present.

2. In order to secure a sample which shall represent the average value of the ash, it is well to take at least 5 grams. As this is too large a quantity for convenient titration, an aliquot portion of the solution is measured off, representing one-fifth of the entire quantity.

It is also possible to weigh out exactly 2.6525 grams of the soda ash, dissolve, filter, and titrate the entire solution, when the number of cubic centimeters of half-normal acid used will indicate directly the alkaline strength in terms of sodium carbonate. The student should verify this statement by calculation.

3. It is customary to dry the soda ash at 110° C. before analysis. Greater uniformity of results is then attainable.

Complete expulsion of the moisture would require a temperature just below the fusion point of the carbonate.

4. The residue insoluble in water must be completely washed to remove soluble alkali, and the filtrate must be cooled to a temperature approximating the laboratory standard before dilution to a definite volume in the measuring flask.

A 50 cc. pipette may equally well be employed to measure out the aliquot portion, in place of the 50 cc. flask.

5. The changes occurring during the titration of the carbonate with an acid are, $2H^+ + CO_3^{--} \rightarrow H_2CO_3 \rightarrow H_2O + CO_2$. The carbonic acid is not only a weak acid but a very unstable compound, and at once breaks down into carbon dioxide and water, the former largely escaping from the solution.

6. The determination of the caustic alkali in the soda ash may be accomplished by precipitating the carbonate with barium chloride, removing it by rapid filtration, and titrating for the alkali in the filtrate. The carbonated alkali is then calculated as the difference between the caustic alkali and the total alkali.

DETERMINATION OF THE ACID STRENGTH OF OXALIC ACID

Procedure.—Weigh out two portions of the acid of about 1 gram each. Dissolve these in 50 cc. of warm water, filter

if the solution is not clear, and wash the filter completely with hot water until freed from oxalic acid. Add to the filtrate two drops of phenolphthalëin solution, and run in alkali from the burette until the solution is pink; add acid from the other burette until the pink is just destroyed, and then add 0.3 cc. (*not more*) in excess. Heat the solution to boiling for three minutes. If the pink returns during the boiling, discharge it with acid and again add 0.3 cc. in excess and repeat the boiling. If the color does not then reappear add alkali until it does, and a *drop or two* of acid in excess and boil again for one minute. If no color reappears during this time, complete the titration in the hot solution. From the corrected volume of alkali required to react with the oxalic acid calculate the weight of the latter present in terms of the crystallized acid ($C_2H_2O_4.2H_2O$), and from this the percentage purity of the sample.

Notes.— 1. It has already been pointed out that it is desirable to employ the same indicator throughout standardization and analysis, a statement which is applicable in this instance. The student is advised, if practicable within the time devoted to the subject, to restandardize acid and alkali, using phenolphthalëin as the indicator, and concluding each titration by boiling the solution as described above, or, what is perhaps better, to standardize the alkali solution against one of the substances named in Note 7, page 97, using phenolphthalëin.

The differences resulting from the change of indicator are small, and the student may neglect them in this instance, performing the titration as outlined above to gain some practice with phenolphthalëin; but it should be remembered that if the highest accuracy is desired, a restandardization throughout is essential.

2. All commercial caustic soda contains some carbonate, and as phenolphthalëin is acted upon by carbonic acid, the solution must be boiled to decompose this. Phenolphthalëin does not show an alkaline reaction with acid carbonates; hence cold, dilute solutions containing carbonates become colorless with this indicator when *half* the carbonate has

been acted upon by acid. Upon boiling, the bicarbonate loses carbon dioxide, forming normal carbonate, and the pink returns. This must be again discharged and the solution boiled, and so on. (Compare page 91.)

It is possible to remove the carbonate from the caustic alkali by the cautious addition of barium hydroxide before standardization; the barium carbonate is removed by filtration.

3. Hydrochloric acid is volatilized from aqueous solutions, except such as are very dilute. If the directions in the procedure are strictly followed no loss of acid need be feared, but the amount added in excess must not exceed 0.3 cc.

4. The end-point should be the faintest visible shade of color (or its disappearance), as the same difficulty would exist here as with methyl orange if an attempt were made to match shades of pink.

II. OXIDATION PROCESSES

GENERAL DISCUSSION

Under this section may properly be included, beside oxidation processes, the rather limited number of methods in which standard solutions of reducing agents are employed, since a corresponding oxidation of the reducing agent must always be a part of the reaction. It may be stated, in general, that *oxidizable* substances are determined by direct titration, while *oxidizing* substances are usually determined by indirect methods.

Many quantitative determinations are made possible by the application of these volumetric methods involving oxidation or reduction, which are not easily practicable by gravimetric procedures. A notable example is that of the determination of iron in the presence of aluminium. The mixture of hydroxides thrown down by ammonia may be ignited, weighed, and the iron subsequently determined volumetrically by solution of the precipitate, reduction of the iron, and oxidation by potassium permanganate or bichromate. The aluminium is then determined by difference.

The important oxidizing agents employed for volumetric solutions are potassium bichromate, potassium permanganate, potassium ferricyanide, iodine, ferric chloride, and sodium hypochlorite.

The important reducing agents which are used in the form of standard solutions are ferrous sulphate (or ferrous ammonium sulphate), oxalic acid, sodium thiosulphate, stannous chloride, arsenious acid, and potassium cyanide. Other reducing agents, as sulphurous acid, sulphureted hydrogen, and zinc (nascent hydrogen), take part in the processes, but not as standard solutions.

The most important combinations among the foregoing are: Potassium bichromate and ferrous salts; potassium permanganate and ferrous salts; potassium permanganate and oxalic acid; iodine and sodium thiosulphate; hypochlorites and arsenious acid.

BICHROMATE PROCESS
## FOR THE DETERMINATION OF IRON

GENERAL DISCUSSION

Ferrous salts may be promptly and completely oxidized to ferric salts, even in cold solution, by the addition of potassium bichromate, provided sufficient acid is present to hold in solution the ferric and chromic compounds which are formed.

The acid may be either hydrochloric or sulphuric, but the former is usually preferred, since it is by far the best solvent for iron and its compounds. The reaction in the presence of hydrochloric acid is as follows: $6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O$.

The ionic changes which occur during processes of oxidation and reduction are somewhat more complicated than those of metathetical reactions such as are usually employed for simple precipitations. This is due largely to the fact that in the cases of oxidation and reduction an ion may change its entire character, and the electrical charges on the new ions may differ both in sign and number from those on the original ions. In equations which express these ionic changes the algebraic sum of the charges must be the same on the two sides.

The changes which are involved in the oxidation of ferrous compounds by means of potassium bichromate in the presence of an acid are most simply expressed by the equation:

$$Cr_2O_7^{--} + 6Fe^{++} + 14H^+ = 2Cr^{+++} + 6Fe^{+++} + 7H_2O.$$
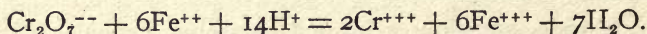
It will be noted that seven oxygen atoms have been removed from the $Cr_2O_7^{--}$-ions and have combined with the H^+-ions to form water; simultaneously there have been formed two Cr^{+++}-ions, and the six Fe^{++}-ions have each acquired an extra positive charge; that is, the $Cr_2O_7^{--}$-ion is reduced and has entirely lost its original character by the withdrawal of its oxygen, while the Fe^{++}-ions are oxidized to Fe^{+++}-ions

by the increase of the electrical charges upon them. The $14H^+$-ions are supplied by the acid added to the solution.

The weight of potassium bichromate necessary for a normal solution was shown on page 76 to be 49.08 grams. It is possible to prepare a standard solution of the bichromate by directly weighing out the requisite quantity and dissolving it in a definite quantity of water. The commercial salt, though rarely sufficiently pure for this purpose as it often contains potassium sulphate, may be purified by recrystallization from hot water, but must then be dried and finally heated to fusion to expel the last traces of moisture. The fusion temperature must not be much exceeded, as the bichromate will lose oxygen if more strongly heated.

It is usually a more satisfactory mode of procedure to prepare a solution from the commercial salt and determine its strength by comparison with iron, either in the form of iron wire of known purity or ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$. A standard wire is offered in the market which answers the purpose well, and its iron contents may be determined for each lot purchased by a number of gravimetric determinations. It may be best preserved in jars containing calcium chloride, but this must not be allowed to come in contact with the wire. It should, however, even then be carefully examined for rust before use.

If ferrous ammonium sulphate is used as the standard, clear crystals only must be selected, and it is perhaps even better to determine by gravimetric methods once for all the iron contents of a sample which has been ground and well mixed. It is well to have on hand a solution of this salt for use in connection with the bichromate. Such a solution is more stable if about 5 cc. of concentrated sulphuric acid per liter are added.

It is plain that all of the iron in the solution must be in the ferrous condition before titration. The available agents for the reduction of ferric iron are stannous chloride, sulphurous acid, sulphureted hydrogen, and zinc; of these stannous chloride acts most readily, the completion of the reaction

is most easily noted, and the excess of the reagent is most readily removed. The latter object is accomplished by oxidation to stannic chloride by means of mercuric chloride added in excess, as the mercury salts have no effect upon ferrous iron or the bichromate. The reactions involved are, $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$; and $SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$. The mercurous chloride is precipitated.

It is essential that the solution should be cold and that the stannous chloride should not be present in great excess, otherwise a secondary reaction takes place, resulting in the reduction of the mercurous chloride to metallic mercury: $SnCl_2 + 2HgCl = SnCl_4 + 2Hg$. The occurrence of this secondary reaction is indicated by the darkening of the precipitate; and since potassium bichromate oxidizes this mercury slowly, solutions in which it has been precipitated are worthless as iron determinations.

The ionic changes involved in this reduction of the iron are: $2Fe^{+++} + Sn^{++} = 2Fe^{++} + Sn^{++++}$. The removal of the excess of the stannous ions depends upon a transfer of charges as follows: $2Hg^{++} + Sn^{++} = Sn^{++++} + 2Hg^{+}$, or, if metallic mercury is thrown out, $Hg^{++} + Sn^{++} = Sn^{++++} + Hg$.

Since no indicator has been found which may be used within the solution, the use of potassium ferricyanide outside the solution is necessary to determine the point at which the ferrous iron is completely oxidized. A drop of the iron solution and one of the indicator solution are brought together on a white surface—best a porcelain tile—and examined for a blue precipitate of the ferrous ferricyanide. It is plain that the potassium ferricyanide must contain no ferrocyanide, for which it should always be carefully tested. The latter, if present, may be oxidized by the addition of a little bromine to the solution, after which the ferricyanide must be recrystallized.

The indicator solution must be very dilute to diminish the interference of its own color; a crystal the size of the head of a pin in 25 cc. of water is an ample quantity. This solution must be freshly prepared each day, as the dilute solution is not stable.

No metals may be present in the titrated solution which, like iron, are reduced by stannous chloride and oxidized by potassium bichromate; notably, copper, antimony, and platinum. For this reason a platinum crucible must never be allowed to remain in a solution of an iron salt in hydrochloric acid, as ferric chloride exerts a slight solvent action upon the platinum.

The bichromate solution may be placed in burettes with rubber tips without danger of deterioration of the solution.

STANDARDIZATION OF A POTASSIUM BICHROMATE SOLUTION

Procedure.—Pulverize about 5 grams of potassium bichromate, dissolve it in water, and dilute to approximately 1000 cc.

Pulverize about 40 grams of ferrous ammonium sulphate, dissolve it in water to which 5 cc. of concentrated sulphuric acid has been added, and dilute to about 1000 cc. It is not necessary to select clear crystals of the sulphate.

Shake the solutions until it is certain that they are uniform, and place them in burettes with the precautions mentioned on page 94.

Prepare a solution of potassium ferricyanide of about the strength recommended above, and place single drops of this solution on the surface of a porcelain tile.

Run out from a burette into a 300 cc. beaker about 40 cc. of the ferrous solution, add 15 cc. of hydrochloric acid (sp. gr. 1.12), dilute it to 150 cc., and run in the bichromate solution from another burette. Since both the solutions are approximately deci-normal, 35 cc. of the bichromate solution may be added without testing. Test at that point by removing a very small drop of the iron solution on the end of a stirring rod and mixing it with a drop of indicator on the tile. If a blue precipitate appears at once, 0.5 cc. of the bichromate solution may be run out before testing again. The stirring rod which has touched the indicator should be dipped in distilled water before returning it to the iron solution. As soon as the blue appears to be less intense add the bichromate solution in small portions, finally a single drop

at a time, until the point is reached at which no blue color appears after the lapse of thirty seconds from the time of mixing solution and indicator on the tile, the time being accurately noted. At the close of the titration a large drop of the iron solution should be taken for the test. To determine the end-point beyond any question, as soon as the thirty seconds have elapsed remove another drop of the solution of the same size as that last taken and mix it with the indicator, placing it beside the last previous test. If this last previous test shows a blue tint in comparison with the fresh mixture, the end-point has not been reached; if no difference can be noted the reaction is complete. Should the end-point be overstepped, more ferrous ammonium sulphate solution may be added.

From the volumes of the solutions used after applying corrections for burette readings, and if need be for the temperature of solutions, calculate the value of the ferrous solution in terms of the oxidizing solution.

Weigh out two portions of iron wire of about 0.24–0.26 gram each, examining the wire carefully for rust. It should be handled and wiped with wash leather—not touched by the fingers—should be weighed on a watch-glass, and be so bent as not to interfere with the movement of the balance.

Place 30 cc. of hydrochloric acid (sp. gr. 1.12) in 300 cc. beakers, cover them with watch-glasses, and bring the acid just to boiling. Remove them from the flame and drop in the portions of wire, taking great care to avoid loss of liquid during the solution. Boil for two or three minutes, keeping the beakers covered; then wash the sides of the beakers and the watch-glass with a little water and add stannous chloride solution to the hot liquid from a dropper until the solution is colorless, but avoid more than a drop or two in excess. Dilute with 150 cc. of water and cool *completely.* When cold add rapidly about 30 cc. of mercuric chloride solution. Allow the solutions to stand about three minutes and then titrate without further delay, as just described. Calculate the volume of the bichromate solution which would be required

if the solution were deci-normal, and add about this quantity.
The ferrous ammonium sulphate solution may be used if the
end-point is passed, and much time saved.

From the corrected volumes of the bichromate solution
required to oxidize the iron actually known to be present in
the wire calculate the value of each cubic centimeter in terms
of iron (Fe), and also the amount of iron in each cubic
centimeter of the ferrous ammonium sulphate solution. Re-
cord these values in the notebook.

Repeat the standardization until the results for the value
of each cubic centimeter in terms of iron are concordant
within 0.00001 gram.

Notes.—1. Note carefully the statements in the "General
Discussion" bearing upon the steps in the standardization.

2. The hydrochloric acid is added to the ferrous solution
to insure the presence of sufficient free acid for the titration,
as required by the equations on page 104.

The solution of the wire in hot acid and the short boiling
insure the removal of compounds of hydrogen and carbon
which are formed from the small amount of carbon in the
iron. These might be acted upon by the bichromate if not
expelled.

3. The time interval for the indicator tests must be care-
fully noted. Some time elapses before the completion of the
reaction with the indicator when the ferrous iron has nearly
all been oxidized, but if left too long the combined effect of
light and dust causes a reduction and a deposition of a blue
precipitate. Thirty seconds is a necessary but also a sufficient
interval.

4. The accuracy of the work may be much impaired by
the removal of unnecessarily large quantities of solution for
the tests. At the beginning of the titration, while much fer-
rous iron is still present, the end of the stirring rod need only
be moist with the solution; but at the close of the titration
drops of considerable size may properly be taken for the final
tests. The stirring rod should be washed to prevent transfer
of indicator to the main solution.

If the end-point is determined as prescribed, it can be as

accurately fixed as that of other methods; and if a ferrous solution is at hand, the titration need consume hardly more time than that of the permanganate process to be described later on.

5. The solution should be allowed to stand about three minutes after the addition of mercuric chloride to permit the complete deposition of mercurous chloride. It should then be titrated without delay to avoid possible reoxidation of the iron by the oxygen of the air.

6. The potassium bichromate solution may be diluted to an exactly deci-normal solution if desired, according to the principles stated on page 96.

DETERMINATION OF IRON IN LIMONITE

Procedure.—Grind the mineral to a fine powder, weigh out two portions of about 0.5 gram into No. 7 porcelain crucibles, heat these crucibles to dull redness for ten minutes, allow them to cool, and place them, with their contents, in beakers containing 30 cc. of hydrochloric acid (sp. gr. 1.12). Heat at a temperature just below boiling until the undissolved residue is white, or until solvent action has ceased; if a dark residue remains, collect it on a filter, wash free from hydrochloric acid, and ignite the filter in a platinum crucible. Mix the ash with five times its weight of sodium carbonate and heat to fusion; cool, and disintegrate the fused mass by boiling water in the crucible. Unite solution and precipitate (if any) with the acid extraction, washing out the crucible; heat the solution to boiling, add stannous chloride solution until it is colorless, avoiding a large excess; cool, and when *cold* add 40 cc. of mercuric chloride solution, and proceed with the titration as already described on page 107.

Calculate the percentage of iron (Fe) in the limonite.

Notes.—1. Limonite is a native, hydrated oxide of iron. It frequently occurs in or near peat beds and contains more or less organic matter which, if brought into solution, would be acted upon by the potassium bichromate. This organic

matter is destroyed by roasting. Since a high temperature tends to lessen the solubility of ferric oxide, the heat should not be raised above low redness.

2. A white residue, or one known to be free from iron, may be neglected and need not be filtered off.

3. The quantity of stannous chloride required for the reduction of the iron in the limonite will be much larger than that added to the solution of iron wire, in which the iron was mainly in the ferrous condition. It should, however, be added from a dropper to avoid an unnecessary excess.

4. The platinum crucible, if used for the carbonate fusion, must not be put into the iron solution. A platinum crucible may also be used for the roasting, if preferred, but with the same precaution with respect to the iron solution.

5. It is sometimes advantageous to dissolve a large portion—say 5 grams—and to take one-tenth of it for titration. The sample will then represent more closely the average value of the ore.

DETERMINATION OF CHROMIUM IN CHROME IRON ORE

Procedure.—Grind the chrome iron ore in an agate mortar until no decided grit is detected when some of the powder is placed between the teeth. Weigh out two portions of 0.5 gram each into iron crucibles which have been scoured inside until bright. Weigh out on the laboratory balances 5 grams of dry sodium peroxide for each portion, and pour about three-quarters of the peroxide upon the ore. Mix ore and flux by thorough stirring with a dry glass rod. Then cover the mixture with the remainder of the peroxide. Place the crucible on a triangle and raise the temperature *slowly* to the melting-point of the flux, using a low flame, and holding the lamp in the hand. Maintain the fusion for five minutes, and stir constantly with a stout platinum wire, but do not raise the temperature above moderate redness.

Allow the crucible to cool until it can be comfortably handled, then place it in a 300 cc. beaker, and cover it with distilled water. The beaker must be carefully covered to avoid loss during the disintegration of the fused mass. When the evolution of gas ceases, rinse off and remove the crucible; then heat the solution to boiling for fifteen minutes. Allow the liquid to cool for a moment; then acidify with dilute sulphuric acid (1 : 5), adding 10 cc. in excess of the amount necessary to dissolve the ferric hydroxide. Dilute to 200 cc., cool, add from a burette an excess of a standard ferrous ammonium sulphate solution, and titrate for the excess with a standard solution of potassium bichromate.

From the corrected volumes of the two standard solutions, and their relations to normal solutions, calculate the percentage of chromium in the ore.

Notes.—1. Chrome iron ore is essentially a ferrous chromite, or combination of FeO and Cr_2O_3. The sodium peroxide acts both as an alkaline flux and as a powerful oxidizing

agent. The chromic oxide is dissolved by the flux and converted to chromic anhydride (CrO_3), which combines with the alkali to form sodium chromate. The iron is oxidized to ferric oxide.

The sodium peroxide cannot be used in porcelain, platinum, or silver crucibles. It attacks iron and nickel as well; but crucibles made from these metals may be used if care is exercised to keep the temperature as low as possible. Preference is here given to iron crucibles, because the resulting ferric hydroxide is more readily brought into solution than the nickelic oxide from the nickel crucible. The peroxide must be dry, and must be protected from any admixture of dust or of organic matter of any kind, otherwise explosions may ensue.

2. When an iron crucible is employed it is desirable to allow the fusion to become nearly cold before it is placed in water, otherwise scales of magnetic iron oxide may separate from the crucible, and by slowly dissolving, after acid is added, reduce the chromate formed.

3. Upon treatment with water the chromate passes into solution, the ferric oxide remains undissolved, and the excess of peroxide is decomposed with the evolution of oxygen. The subsequent boiling insures the complete decomposition of the peroxide, which would otherwise react with the chromate when the solution is acidified.

4. The addition of the sulphuric acid converts the sodium chromate to bichromate, which behaves exactly like potassium bichromate in acid solution; therefore three atoms of iron are oxidized for each atom of chromium: $Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O$; $2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$; $6FeSO_4 + Na_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Na_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$.

The ionic changes involved in this procedure are the same as those given on page 104. The change from the chromate to the bichromate may be expressed thus:

$$2CrO_4^{--} + 2H^+ = Cr_2O_7^{--} + (H_2O).$$
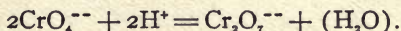
5. If a standard solution of a ferrous salt is not at hand, a weight of iron wire somewhat in excess of the amount

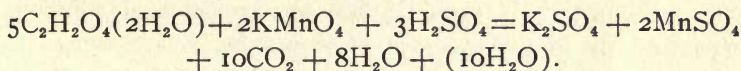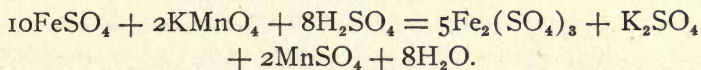which would be required if the chromite were pure FeO. Cr_2O_3 may be weighed out and dissolved in acid; after reduction of all the iron is assured, this solution may be poured into the chromate solution and the excess of iron determined by titration with standard bichromate solution.

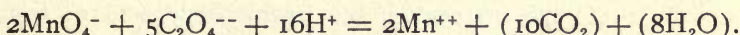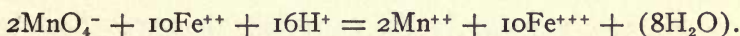## PERMANGANATE PROCESS FOR THE DETERMINATION OF IRON

GENERAL DISCUSSION

Potassium permanganate oxidizes ferrous salts, in cold, acid solution, promptly and completely to the ferric condition, while in hot, acid solution it also enters into a definite reaction with oxalic acid by which the latter is oxidized to carbon dioxide and water.

The reactions involved are these:

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

$$5C_2H_2O_4(2H_2O) + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O + (10H_2O).$$

The corresponding ionic changes are most simply expressed as:

$$2MnO_4^- + 10Fe^{++} + 16H^+ = 2Mn^{++} + 10Fe^{+++} + (8H_2O).$$

$$2MnO_4^- + 5C_2O_4^{--} + 16H^+ = 2Mn^{++} + (10CO_2) + (8H_2O).$$

These are the fundamental reactions upon which the extensive use of potassium permanganate depends; but beside iron and oxalic acid the permanganate enters into reaction with antimony, tin, copper, mercury, and manganese (the latter only in neutral solution), by which these metals are changed from a lower to a higher state of oxidation; and it also reacts with sulphurous acid, sulphureted hydrogen, nitrous acid, ferrocyanides, and most soluble organic bodies. It should be noted, however, that very few of these organic compounds react in as definite a way with the permanganate as is the case with oxalic acid and the oxalates.

From the definition of a normal oxidizing solution (page 76) the normal solution of potassium permanganate for use in the presence of acid must contain 31.63 grams of the reagent. This is seen from the following considerations: Two molecules of the permanganate yield, as shown in the equations above, one molecule of potassium salt correspond-

ing to the oxide K_2O, and two molecules of manganous salt corresponding to the oxide MnO, leaving five available oxygen atoms ($2KMnO_4 = K_2O + 2MnO + 5O$). The five oxygen atoms furnished by the two gram-molecules of the permanganate (316.3 grams) are equivalent to 10 grams of hydrogen. Accordingly, the normal solution must contain one-tenth of two gram-molecules or one-fifth of one gram-molecule; *i. e.*, 31.63 grams.

In neutral solution the permanganate is decomposed in the way indicated by the equation, $2KMnO_4 = K_2O + 2MnO_2 + 3O$. The normal solution for such purposes should contain one-sixth of two gram-molecules; that is, 52.71 grams.

Potassium permanganate is acted upon by hydrochloric acid; the action is rapid in hot or concentrated solutions (particularly in the presence of iron salts, which appear to act as catalyzers, increasing the velocity of the reaction), but slow in cold, dilute solutions. The use of the permanganate in the presence of hydrochloric acid or its salts may therefore be attended by the possibility of error, and it is usually preferable to replace the hydrochloric acid of iron solutions by sulphuric acid before titration. This may be accomplished by evaporating with an excess of the latter until the heavy, white fumes of sulphuric anhydride appear.

The greater solubility of iron compounds in hydrochloric acid makes it desirable to titrate, if possible, directly in such solutions; and experiments made with this end in view have shown that in cold, dilute hydrochloric acid solutions, to which considerable quantities of manganous sulphate or chloride and an excess of phosphoric acid have been added, it is possible with practice to obtain satisfactory results; but the end-point is less permanent than in sulphuric acid solutions. Such a process is described in the *J. Am. Chem. Soc.*, **17**, 405.

Potassium permanganate has an intense coloring power, and since the solution resulting from the oxidation of the iron and the reduction of the permanganate is colorless, the latter becomes its own indicator. The slightest excess is indicated with great accuracy by the color of the solution,

which renders the titration one of the most satisfactory known. The commercial salt is rarely sufficiently pure to admit of direct weighing to prepare a standard solution, but it may be purified by recrystallization. The more common practice is to standardize the solution, which may be accomplished by comparison with iron wire, ferrous ammonium sulphate, oxalic acid, potassium tetroxalate, or potassium acid oxalate. Other substances have been proposed, but the foregoing are the ones in common use.

The remarks on page 105 referring to the use of iron wire and ferrous ammonium sulphate apply with equal force here. The pure oxalic acid or the oxalates must be freshly prepared and with great care; they are likely to lose water of crystallization on standing. It must also be borne in mind that the reaction with the oxalates takes place only in hot solution.

The reducing agents available for the necessary reduction of the iron before titration are zinc, sulphurous acid, or sulphureted hydrogen; stannous chloride is excluded unless the titration is to be made in the presence of hydrochloric acid. Since the excess of both the gaseous reducing agents can only be expelled by boiling, with consequent uncertainty regarding the reoxidation of the iron, zinc is the more satisfactory agent; but for prompt and complete reduction it is essential that the solution should be brought into intimate contact with the zinc. This is brought about by the use of a modified Jones reductor,[1] as shown in Figure 3.

To prevent needless consumption of the zinc, it is first amalgamated by dissolving 5 grams of mercury in 25 cc. of concentrated nitric acid, diluted with an equal bulk of water, and pouring into this solution (diluted to 250 cc. in a 1000 cc. flask) 500 grams of granulated zinc, 20–30 mesh. The whole is shaken thoroughly for two minutes, the solution poured off, and the zinc carefully washed. It may then be preserved in bottles.

[1] The details of the reductor and preparation of the zinc are taken from Blair's *Chemical Analysis of Iron*, page 95, *et seq.*

The tube *A* has an inside diameter of 18 mm. and is 300 mm. long; the small tube has an inside diameter 6 mm. and extends 100 mm. below the stopcock. At the base of the tube *A* are placed some pieces of broken glass, covered by a plug of glass wool about 8 mm. thick, and upon this is placed
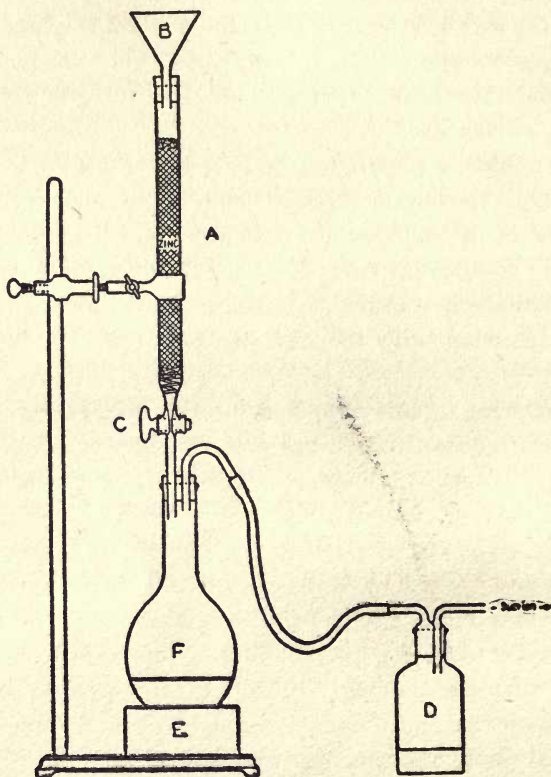

FIG. 3

a thin layer of asbestos, such as is used for Gooch filters, 1 mm. thick. The tube is then filled with the amalgamated zinc to within 50 mm. of the top, and on the zinc is placed a plug of glass wool. The 60 mm. funnel *B* is fitted into the tube with a rubber stopper, and the reductor is connected with a suction bottle, *F*. The bottle *D* is a safety bottle to prevent contamination of the solution by water from the pump.

The iron solution during its passage through the reductor comes into intimate contact with the zinc, and is reduced by it or by the nascent hydrogen evolved. The column of zinc should never be less than 15 cm. in length. *Great care* must be used to prevent the access of air to the reductor after it has been washed out ready for use. If air enters, hydrogen peroxide forms which reacts with the permanganate, and the results are worthless.

It is also possible to reduce the iron by treatment with zinc in a flask from which air is excluded, the zinc being finally completely dissolved. This method is, however, less convenient and more tedious than the reductor.

Potassium permanganate solutions are not usually stable for long periods, and change more rapidly when first prepared than after standing some days. This is probably caused by interaction with the organic matter contained in all distilled water, except that redistilled from an alkaline permanganate solution. The solutions should, however, be protected from the light and heat as far as possible, since both induce decomposition with a deposition of manganese dioxide; and it has been shown[1] that the decomposition proceeds with considerable rapidity, with the evolution of oxygen, after the dioxide has begun to form. As commercial samples of the permanganate are likely to be contaminated by the dioxide, it is advisable to filter solutions through asbestos before standardization. Such solutions are relatively stable.

The permanganate solution cannot be placed in burettes with rubber tips, as a reduction takes place upon contact with the rubber. The solution has so deep a color that the lower line of the meniscus cannot be detected; readings must therefore be made from the upper edge.

STANDARDIZATION OF A POTASSIUM PERMANGANATE SOLUTION

Procedure.—Dissolve about 3.25 grams of potassium permanganate crystals in 200 cc. of water in a beaker, warm-

[1] Morse, Hopkins, and Walker, *Am. Chem. J.,* **18**, 401.

ing to hasten solution. Filter through a layer of asbestos, cool, dilute to about 1000 cc., and mix thoroughly. Fill a glass-stoppered burette with this solution, observing the usual precautions, and fill a second burette with the ferrous ammonium sulphate solution prepared for use with the potassium bichromate. Run out into a beaker about 40 cc. of the iron solution, add 10 cc. of dilute sulphuric acid (1 : 5), and run in the permanganate solution to a slight permanent pink. Repeat, until the ratio of the two solutions is satisfactorily established.

Weigh out into beakers two portions of iron wire of about 0.25 gram each. Dissolve these in hot, dilute sulphuric acid (5 cc. of concentrated acid and 100 cc. of water), using a covered flask to avoid loss by spattering. Boil the solution for two or three minutes after the iron is dissolved to remove any volatile hydrocarbons. Meanwhile prepare the reductor for use as follows: Connect the suction bottle with the vacuum pump, fill the reductor while the stopcock is closed (or nearly so) with warm, dilute sulphuric acid (5 cc. of acid in 100 cc. water), and then open the stopcock so that the acid runs through slowly. Continue to pour in acid until 200 cc. have passed through, then close the cock *while a small quantity of liquid is still left in the funnel.* Remove the filtrate, and again pass through 100 cc. of the warm, dilute acid. Test this with the permanganate solution. A single drop should color it permanently; if it does not, repeat the washing. Be sure that no air enters the reductor.

Pour the iron solution while hot (but not boiling) through the reductor at a rate not exceeding 50 cc. per minute. Wash out the beaker with dilute sulphuric acid, and follow the iron solution without interruption with 175 cc. of the warm acid and finally with 75 cc. of distilled water, leaving the funnel partially filled. Remove the filter bottle and cool the solution quickly under the water tap, avoiding unnecessary exposure to the oxygen of the air. Add 10 cc. of dilute sulphuric acid and titrate to a faint pink with the permanganate solution, adding it directly to the contents of the filter

bottle. Should the end-point be overstepped, the ferrous ammonium sulphate solution may be added. From the volume of the solution required to oxidize the iron in the wire, calculate the value of each cubic centimeter in terms of metallic iron (Fe) after applying the usual corrections. The results should be concordant within 0.00001 gram.

Notes.—1. A careful study of the "General Discussion" should be made in connection with the steps of this and the following procedure.

2. The funnel of the reductor must never be allowed to empty, and if it is left partially filled, the reductor is ready for subsequent use after a very little washing; but a preliminary test is always necessary to safeguard against error.

If more than a small drop of permanganate solution is required to color 100 cc. of the dilute acid after the reductor is well washed, an allowance must be made for the iron in the zinc.

The rate at which the iron solution passes through the zinc should not exceed that prescribed, but the rate may be increased somewhat when the wash-water is added. It is well to allow the iron solution to run nearly, but not entirely, out of the funnel before the wash-water is added. If it is necessary to interrupt the process, the complete emptying of the funnel can always be avoided by closing the stopcock.

It must be borne in mind that it is only the zinc or the *nascent* hydrogen which is efficient as a reducing agent. That which is visible is molecular hydrogen and without influence upon the ferric iron.

3. The dilute sulphuric acid for washing must be warmed ready for use before the reduction of the iron begins, and it is of the first importance that the volume of acid and of wash-water should be measured, and that the volume used should always be the same in the standardizations and all subsequent analyses.

4. The end-point is more permanent in cold than hot solutions, possibly because of a slight action of the permanganate upon the manganous sulphate formed during the titration. .If the solution turns brown, it is an evidence of insufficient acid, and more should be immediately added. The

results are likely to be less accurate in this case, however, as a consequence of secondary reactions between the ferrous iron and the manganese dioxide thrown down.

5. The potassium permanganate may, of course, be diluted and brought to an exactly $\frac{N}{10}$ solution from the data here obtained. The percentage of iron in the iron wire must be taken into account in all calculations.

DETERMINATION OF IRON IN LIMONITE

Procedure.—Weigh out two portions of the powdered limonite, roast, and bring them into solution as described on page 110, but dissolve finally in casseroles. Add to the solution, cautiously, 6 cc. of concentrated sulphuric acid and evaporate on the steam bath until the solution is nearly colorless. Cover the casseroles and heat over the flame of the lamp until the heavy white fumes of sulphuric anhydride are freely evolved. Cool the casseroles, add 100 cc. of water (measured), and boil gently until the ferric sulphate is dissolved; pour the warm solution through the reductor, proceed as described under standardization, taking pains to use the same volume and strength of acid and the same volume of wash-water as there prescribed, and titrate with the permanganate solution in the filter flask, using the ferrous ammonium sulphate solution if the end-point should be overstepped. From the corrected volume of permanganate solution used, calculate the equivalent quantity of iron (Fe) and the percentage in the limonite.

> *Notes.*—1. The preliminary roasting is probably necessary, even though the sulphuric acid subsequently chars the carbonaceous matter. Certain nitrogenous bodies are not rendered insoluble in the acid, and would be oxidized by the permanganate.
>
> 2. The hydrochloric acid, both free and combined, is displaced by the less volatile sulphuric acid at its boiling point. The ferric sulphate separates at this point, since there is no water to hold it in solution, and care is required to prevent bumping.

3. The ferric sulphate usually has a silky appearance and is easily distinguished from the flocculent silica which often remains undissolved. A small quantity of glass wool may be placed in the neck of the funnel to prevent the passage of this silica into the reductor.

4. Iron ores containing titanium cannot be treated as described above, because the titanium salts are reduced during the passage through the reductor and are oxidized by the permanganate. The iron in solutions of titaniferous ores must be reduced by means of hydrogen sulphide or sulphurous acid, neither of which reduces titanium compounds.

DETERMINATION OF THE OXIDIZING POWER OF PYROLUSITE

Pyrolusite, when pure, consists of manganese dioxide. Its value as an oxidizing agent, and for the production of chlorine, depends upon the percentage of MnO_2 in the sample. This percentage is determined by an indirect method, in which the manganese dioxide may be reduced and dissolved by an excess of ferrous sulphate or oxalic acid, and the unused excess determined by titration with permanganate.

Procedure.—Grind the mineral in an agate mortar until no grit whatever can be detected when the powder is placed between the teeth. Dry the ground sample on a watch-glass at 110° C. for an hour, transfer it to a stoppered weighing-tube, and weigh out two portions of about 0.5 gram into 300 cc. beakers. Calculate the weight of oxalic acid ($C_2H_2O_4.2H_2O$) required to react with the weights of pyrolusite taken for analysis, assuming it to be pure manganese dioxide: $MnO_2 + C_2H_2O_4(2H_2O) + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O$. Weigh out about 0.2 gram in excess of this quantity of *pure* oxalic acid into the corresponding beakers, weighing the acid accurately and recording the weight in the notebook. Cover the beakers and pour into each 25 cc. of water and 50 cc. of dilute sulphuric acid (1 : 5), and warm the liquid gently until the evolution of carbon dioxide ceases. If a residue remains which is sufficiently colored to obscure the end-reaction of the permanganate it must be removed by filtration.

Finally, heat the solution to a temperature just below boiling, and while hot, titrate for the excess of the oxalic acid with potassium permanganate solution. From the corrected volume of the solution required, calculate the amount of oxalic acid undecomposed by the pyrolusite; subtract this from the total quantity of acid used, and calculate the weight of manganese dioxide which would react with the balance of the acid, and from this the percentage in the sample. Consult Part IV, page 143.

Notes.—1. The success of the analysis is largely dependent upon the fineness of the powdered mineral. If properly ground, solution should be complete in fifteen minutes or less.

2. The ground pyrolusite is somewhat hygroscopic. It should be dried at a low temperature (110°), as a higher heat tends to expel water of constitution from hydrated oxides which may also be present.

3. A moderate excess of oxalic acid above that required to react with the pyrolusite is necessary to promote solution; otherwise the residual quantity of oxalic acid would be so small that the last particles of the mineral would scarcely dissolve. It is also desirable that a sufficient excess of the acid should be present to react with a considerable volume of the permanganate solution during the titration.

4. Care should be taken that the sides of the beaker are not overheated, as oxalic acid would be decomposed by heat alone if crystallization should occur on the sides of the vessel. Strong sulphuric acid also decomposes the oxalic acid. The dilute acid should, therefore, be prepared before it is poured into the beaker.

5. Ferrous ammonium sulphate or iron wire may be substituted for the oxalic acid. The reaction is then the following: $2FeSO_4 + MnO_2 + 2H_2SO_4 = Fe_2(SO_4)_3 + MnSO_4 + 2H_2O$. The excess of ferrous iron may also be determined by means of potassium bichromate, if desired. The ionic changes are similar to those given on page 115: $(MnO_2) + 2Fe^{++} + 4H^+ = Mn^{++} + 2Fe^{+++} + (2H_2O)$.

Care is required to prevent the oxidation of the iron by the air, if ferrous salts are employed.

6. Other volumetric processes may be employed for this determination, one of which is outlined in the following reactions: $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$; $Cl_2 + 2KI = I_2 + 2KCl$; $I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$. The chlorine generated by the pyrolusite is passed into a solution of potassium iodide. The liberated iodine is then determined by titration with sodium thiosulphate, as described on page 129. This is a direct process, although it involves three steps.

It is also possible to absorb and weigh the liberated carbon dioxide evolved during the reaction with the oxalic acid, and from this weight to find the percentage of manganese dioxide in the sample. This is a gravimetric process.

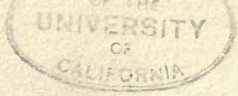## IODIMETRY

GENERAL DISCUSSION

The titration of iodine against sodium thiosulphate, with starch as an indicator, may perhaps be regarded as the most accurate of volumetric processes. It may be used both in acid and in neutral solutions to measure free iodine, and the latter may, in turn, serve as a measure of any substance capable of liberating iodine from potassium iodide under suitable conditions for titration. For example, the quantity of potassium bromate in a commercial sample of that salt may be determined through the following reactions: $KBrO_3 + 6KI + 3H_2SO_4 = 3K_2SO_4 + KBr + 3I_2 + 3H_2O$, and $I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$.

Another illustration is afforded by the process outlined in Note 6, page 125.

Iodine is an oxidizing agent, and as such must conform to the same conditions as other similar bodies with respect to its normal solution. From the equation, $SO_2 + I_2 + H_2O = SO_3 + 2HI$, it is plain that 126.97 grams of iodine suffice to displace an amount of oxygen equivalent to 1 gram of hydrogen, and accordingly that weight of iodine is requisite for a normal solution. Deci- and centi-normal iodine solutions are commonly used.

Iodine acts as an oxidizing agent either through the decomposition of water in the presence of an oxidizable body, as illustrated by the reaction, $Na_3AsO_3 + I_2 + H_2O = Na_3AsO_4 + 2HI$, or by increasing the proportion of the negative constituent of a compound through the direct withdrawal of the positive component, as typified by the equations: $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$, and $H_2S + I_2 = 2HI + S$.

The ionic changes involved in three of the above typical reactions in which iodine is employed as a standard solution may be most simply expressed as follows: $BrO_3^- + 6I^- + 6H^+ = Br^- + (3I_2) + (3H_2O)$; $2S_2O_3^{--} + (I_2) = 2I^- + S_4O_6^{--}$; $AsO_3^{---} + (I_2) + 2OH^- = AsO_4^{---} + 2I^- + (H_2O)$.

A complete equipment for iodimetric work requires solutions of iodine, sodium thiosulphate, potassium iodide, and starch.

Commercial iodine requires resublimation before it can be regarded as sufficiently pure to be used as the basis of a standard solution. It should be sublimed between watchglasses after the addition of potassium iodide to unite with any chlorine present in combination with the iodine, and should be subsequently dried over sulphuric acid. It may then be dissolved, in a stoppered flask, in a solution of potassium iodide (about 18 grams of the iodide to 12 of the iodine) and diluted to a definite volume.

Its solutions are decomposed by sunlight, with the formation of hydriodic acid, and even a high room-temperature tends to volatilize the iodine. They are not stable for long periods, and require frequent standardization against pure arsenious acid, anhydrous sodium thiosulphate, or standard solutions of the latter.

Iodine solutions act upon rubber; hence only burettes with glass stopcocks should be used.

Sodium thiosulphate ($Na_2S_2O_3.5H_2O$) is rarely wholly pure as sold commercially, but may be purified by crystallization. The carbon dioxide absorbed from the air by distilled water decomposes the salt, with the separation of sulphur; and if standard solutions are to be prepared by dissolving the pure salt, boiled water which has been cooled out of contact with the air must be used.

Solutions of the thiosulphate must be protected from light and heat, both of which promote decomposition. They may be standardized against pure iodine, or—with the help of potassium iodide—against potassium bromate, potassium iodate, or potassium bichromate. The reactions on page 126 indicate the principle involved.

It should be noted that chlorine and bromine oxidize the thiosulphate to sulphate, while the iodine forms sodium tetrathionate, $Na_2S_4O_6$.

Commercial potassium iodide generally contains a small

quantity of iodate, which in acid solution liberates iodine, as indicated by a yellow coloration of these solutions. The reaction is: $KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + 3I_2 + 3H_2O$. The iodate is not necessarily uniformly distributed through the iodide, and in order that an accurate blank test for iodate may be made which can be applied to each analysis in which it is used, it is necessary to bring a considerable quantity of the iodide into solution and to take a measured volume of this solution for each analysis. The strength of such a solution is adjusted to the conditions of its use.

The starch solution for use as an indicator must be freshly prepared. A soluble starch is now obtainable which serves well, and a solution of 0.5 gram of this starch in 25 cc. of boiling water is sufficient. It is ready for use when cold, and from 1 cc. to 2 cc. suffices.

If soluble starch is not at hand potato starch may be used. Mix about 1 gram with 5 cc. of cold water to a smooth paste, pour 150 cc. of *boiling* water over it, warm for a moment on the hot plate, and put it aside to settle. Decant the supernatant liquid through a filter and use the clear filtrate; 5 cc. of this solution are needed for a titration.

The solution of potato starch is less stable than the soluble starch. The solid particles of the starch if not removed become so colored by the iodine that they are not readily decolorized by the thiosulphate.

The iodo-starch blue is discharged by caustic alkalies and somewhat less readily by normal carbonates of the fixed alkalies, but not by the bicarbonates.

STANDARDIZATION OF IODINE AND SODIUM THIOSULPHATE SOLUTIONS

Procedure.—Weigh out on the laboratory balances 13 grams of commercial iodine. Place it in a mortar with 18 grams of potassium iodide and triturate with small portions of water until all is dissolved. Dilute the solution to 1000 cc.[1]

---

[1] It will be found more economical to have a considerable quantity of the solution prepared by a laboratory attendant, and to have all unused solutions returned to the common stock.

Weigh out 25 grams of sodium thiosulphate, dissolve it in water, and dilute to 1000 cc.

Place these solutions in burettes (the iodine in a glass-stoppered burette), observing the usual precautions to prevent dilution. Run out 40 cc. of the thiosulphate solution into a beaker, dilute with 150 cc. of water, add 1 cc. to 2 cc. of the soluble starch solution, and titrate with the iodine to the appearance of the blue of the iodo-starch. Repeat until the ratio of the two solutions is established, remembering all necessary corrections for burettes and for temperature changes.

This.

(*Method A*)

Weigh out into 500 cc. beakers two portions of 0.175–0.200 gram each of pure arsenious oxide. Dissolve these in 10 cc. of sodium hydroxide solution, with stirring. Dilute the solutions to 150 cc. and add hydrochloric acid until the solution contains a few drops in excess, and finally add a concentrated solution of 5 grams of pure sodium bicarbonate ($HNaCO_3$). Cover the beakers before adding the bicarbonate to avoid loss. Add the starch solution and titrate with the iodine to the appearance of the blue of the iodo-starch, taking care not to pass the end-point.

From the corrected volume of the iodine solution used to oxidize the arsenious oxide, calculate the quantity of iodine in each cubic centimeter and its relation to the normal. From the ratio between the solutions, calculate similar values for the thiosulphate solution.

(*Method B*)

Weigh out into 500 cc. beakers two portions of about 0.150–0.175 gram of potassium bromate or potassium iodate. Dissolve these in 50 cc. of water, and add a sufficient volume of potassium iodide solution to contain 3 grams of the salt. Add to the mixture 10 cc. of dilute sulphuric acid (1 : 5), allow the solution to stand for three minutes, and dilute to 150 cc.; run in thiosulphate solution from a burette until the color of the liberated iodine is nearly destroyed, then add

1 cc. or 2 cc. of starch solution, titrate to the disappearance of the iodo-starch blue, and finally add iodine solution until the color is just restored. Make a blank test for the amount of thiosulphate solution required to react with the iodine liberated by the iodate in the potassium iodide solution, and deduct this from the total volume used in the titration. From the data obtained, calculate the weight of thiosulphate in each cubic centimeter of the solution and its relation to a normal solution, and subsequently calculate similar values for the iodine solution.

Notes.—1. The two methods of standardization seem to yield equally satisfactory results, and the student is advised to try both. The arsenious oxide and the potassium salts both require careful examination to establish their purity. The former usually requires resublimation, and the two latter recrystallization.

2. The color of the iodo-starch is somewhat less satisfactory in concentrated solutions of alkali salts, notably the iodides. The dilution prescribed obviates this difficulty.

3. Arsenious oxide dissolves more readily in caustic alkali than in the bicarbonates, but the presence of caustic alkali during the titration is not admissible. It is therefore destroyed by the addition of acid, and the solution is then made alkaline with the bicarbonate.

The reaction during titration is the following:

$$Na_3AsO_3 + I_2 + 2HNaCO_3 = Na_3AsO_4 + 2NaI$$
$$+ 2CO_2 + H_2O.$$
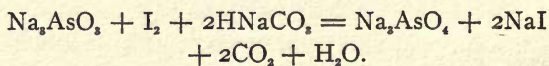
As the reaction between sodium thiosulphate and iodine is not always free from secondary reactions in the presence of even the weakly alkaline bicarbonate, it is best to avoid the addition of any considerable excess of iodine. Should the end-point be passed by a few drops, the thiosulphate may be used to correct it.

4. The potassium iodide should be measured from a stock solution for the reasons stated on page 128. It is then possible to make an accurate blank test for the iodate.

DETERMINATION OF ANTIMONY IN STIBNITE

The sample for analysis should preferably be pure, or leave at most only a siliceous residue.

Procedure.—Weigh out two portions of about 0.35–0.40 gram of the mineral (which should be well ground) into two small, dry beakers (100 cc.). Cover the beakers and pour over the stibnite 5 cc. of hydrochloric acid (sp. gr. 1.20) and warm gently on the water bath. When the residue is white, add to each 2 grams of powdered tartaric acid. Warm the solution on the water bath for ten minutes longer, dilute the solution very cautiously by adding water in portions of 5 cc., stopping if the solution turns red. It is possible that no coloration will appear, in which case cautiously continue the dilution to 125 cc. If a red precipitate or coloration does appear, warm the solution until it is colorless, and again dilute cautiously to a total volume of 125 cc. and boil for a minute.

Carefully neutralize most of the acid with ammonium hydroxide solution (sp. gr. 0.96), but leave it distinctly acid. Dissolve 3 grams of sodium bicarbonate in 200 cc. of water in a 700 cc. beaker, and pour the cold solution of the antimony chloride into this, avoiding loss by effervescence. Make sure that the solution contains an excess of the bicarbonate, and then add 1 cc. or 2 cc. of starch solution and titrate with iodine solution to the appearance of the blue, avoiding an excess.

From the corrected volume of the iodine solution required to oxidize the antimony calculate the weight of the latter in the solution and the percentage in the stibnite.

Notes.—1. The success of this determination is largely dependent upon close adherence to the directions as given, particularly with respect to the amounts of reagents and the dilutions.

2. Antimony chloride is volatile with the steam from its concentrated solutions; hence these solutions must not be boiled until they have been diluted.

3. Antimony salts, such as the chloride, are readily hydro-

lyzed, and compounds of the character of SbOCl are formed which are often relatively insoluble; but in the presence of tartaric acid compounds with complex ions are formed, and these are soluble. An excess of hydrochloric acid also prevents precipitation of the oxychloride because the H^+-ions from the acid lessen the dissociation of the water and thus prevent any considerable hydrolysis.

4. Stibnite is native antimony sulphide, and upon solution in hydrochloric acid sulphureted hydrogen is liberated, a part of which is absorbed by the acid. This is usually expelled by the heating upon the water bath; but if it is not wholly driven out, a point is reached during dilution at which the antimony sulphide, being no longer held in solution by the acid, separates. If the dilution is immediately stopped and the solution warmed, this sulphide is again brought into solution and at the same time more of the sulphureted hydrogen is expelled. This procedure must be continued until the sulphureted hydrogen is all removed, since it reacts with iodine.

If no precipitation of the sulphide occurs, it is an indication that it was all expelled after solution.

5. If, for any reason, a white precipitate of the oxychloride separates during dilution (which should not occur if the directions are followed), it is best to discard the determination and to start anew.

6. The reaction between the iodine and the antimony compounds which are formed in the presence of the tartaric acid is probably somewhat complex. For purposes of calculation it may be regarded as parallel with that given in Note 3, page 130, substituting sodium antimonite, Na_3SbO_3, for sodium arsenite.

7. If the end-point is not permanent, that is, if the blue of the iodo-starch is discharged after standing a few moments, the cause may be an insufficient quantity of sodium bicarbonate, leaving the solution slightly acid, or a slight precipitation of an antimony compound, which is slowly acted upon by the iodine when the latter is momentarily in excess. In either case it is better to discard the analysis and to repeat the process, using greater care in the amounts of reagents employed.

The ammonium hydroxide is added merely to neutralize a portion of the acid, thus reducing the amount of bicarbonate required. It must not be added in sufficient quantity to neutralize all of the acid.

CHLORIMETRY

GENERAL DISCUSSION

The processes included under the term chlorimetry comprise those employed to determine chlorine, hypochlorites, bromine, and hypobromites. The reagent employed is sodium arsenite in the presence of sodium bicarbonate. The reaction in the case of the hypochlorites is, $NaClO + Na_3AsO_3 = Na_3AsO_4 + NaCl$; or $ClO^- + AsO_3^{---} = AsO_4^{---} + Cl^-$.

The sodium arsenite may be prepared from pure arsenious oxide, as described below, and is stable for considerable periods; but the commercial oxide requires resublimation to remove arsenic sulphide, which may be present in small quantity. To prepare the solution, dissolve about 5 grams of the powdered oxide, accurately weighed, in 10 cc. of a concentrated sodium hydroxide solution, dilute the solution to 300 cc., and make it faintly acid with hydrochloric acid. Add 30 grams of sodium bicarbonate, and dilute the solution to 1000 cc. in a measuring flask. If desired, the value of this solution may be checked by titration against a standardized iodine solution.

The indicator required is made by dipping strips of filter paper in a starch solution prepared as described on page 128, to which 1 gram of potassium iodide has been added. These strips are allowed to drain and spread upon a watch-glass. When touched by a drop of the solution, the paper turns blue until the hypochlorite has all been reduced and an excess of the arsenite has been added. The paper must be moist when used.

DETERMINATION OF THE AVAILABLE CHLORINE IN BLEACHING POWDER

Procedure.—Weigh out from a stoppered test tube into a porcelain mortar about 3.5 grams of bleaching powder. Keep the mortar away from the door of the balance-case to avoid injury to the balance. Triturate the powder in the mortar with successive portions of water until it is well

ground and washed into a 500 cc. measuring flask. Fill the flask to the mark and shake thoroughly. Measure off 25 cc. of this semi-solution in a measuring flask, or pipette, observing the precautions named on page 46, and the further precaution that the liquid removed shall contain approximately its proportion of suspended matter.

Empty the flask into a beaker and wash it out. Run in the arsenite solution from a burette until no further reaction takes place on the starch-iodide paper when touched by a drop of the solution of bleaching powder. From the volume of solution required to react with the bleaching powder, calculate the percentage of available chlorine in the latter, assuming the titration reaction to be that between chlorine and arsenious oxide, $As_4O_6 + 4Cl_2 + 4H_2O = 2As_2O_5 + 8HCl$. Note that only one-twentieth of the total weight of bleaching powder enters into the reaction.

Notes.—1. Bleaching powder may be regarded as containing both calcium chloride and hypochlorite. Its efficiency when treated with acids depends upon the quantity of the latter constituent, since the hypochlorous acid yields as bleaching agents both oxygen and chlorine. It is customary, however, to express the value of the bleaching agent in terms of available chlorine, as though only that were a factor in its efficiency. The chlorine present as chloride is, of course, not available for bleaching purposes.

2. Bleaching powder readily loses chlorine on exposure to the air, as a result of the absorption of carbon dioxide and the consequent liberation of the very weak hypochlorous acid by the carbonic acid formed. The sample must be carefully protected, but even then it is rarely possible to obtain closely agreeing results from separate samples. For technical purposes it is usually sufficient to examine one sample. The student should check his results by titrating two 25 cc. portions from the 500 cc.

3. The powder must be triturated until it is fine, otherwise the lumps will inclose calcium hypochlorite, which will fail to react with the arsenious acid. The clear supernatant liquid gives percentages which are below, and the sediment

percentages which are above, the average. The liquid measured off should, therefore, carry with it its proper proportion of the sediment, so far as that can be brought about by shaking the solution just before removal of the aliquot part for titration.

III. PRECIPITATION METHODS

THE DETERMINATION OF SILVER BY THE THIOCYANATE PROCESS

GENERAL DISCUSSION

THE addition of a solution of potassium or ammonium thiocyanate to one of silver in nitric acid causes a deposition of silver thiocyanate as a white, curdy precipitate. If ferric nitrate is also present, the slightest excess of the thiocyanate over that required to combine with the silver is indicated by the deep red which is characteristic of the thiocyanate test for iron.

The reactions involved are: $AgNO_3 + KSCN = AgSCN + KNO_3$, and $3KSCN + Fe(NO_3)_3 = Fe(SCN)_3 + 3KNO_3$.

The corresponding ionic reactions are: $Ag^+ + SCN^- = AgSCN$ and $Fe^{+++} + 3SCN^- = [Fe(SCN)_3]$. The ferric thiocyanate differs from the great majority of salts in that it is but very little dissociated in aqueous solutions, and the characteristic color appears to be occasioned by the formation of the un-ionized ferric salt.

The normal solution of the thiocyanate should contain a sufficient quantity of the salt to combine with 1 gram of hydrogen to form thiocyanic acid; that is, a gram-molecule, or 97.22 grams KSCN. The thiocyanate cannot be accurately weighed; its solutions must, therefore, be standardized against silver nitrate, either in the form of a standard solution or by weighing out small portions. An $\frac{N}{20}$ solution of the thiocyanate is the strength to be used for titrations.

The reaction with silver may be carried out in nitric acid solution and in the presence of copper, if the latter does not exceed 70 per cent. Above that percentage it is necessary to add silver in known quantity to the solution.

The liquid must be cold at the time of titration and entirely free from nitrous compounds.

A saturated solution of ferric alum to which a moderate

quantity of nitric acid has been added serves as an indicator. The volume used is 5 cc. and should be the same for each titration.

STANDARDIZATION OF A POTASSIUM THIOCYANATE SOLUTION

Procedure.—Crush a few crystals of silver nitrate in a mortar, transfer them to a watch-glass, and dry for an hour at 110° C. Protect the nitrate from dust or organic matter. Weigh out two portions of about 0.5 gram each. Dissolve these in 50 cc. of water, and add 10 cc. of nitric acid (sp. gr. 1.2) which has been recently boiled, and 5 cc. of the indicator solution. Run in the thiocyanate solution from a burette until a faint red tinge can be detected in the solution, after vigorous stirring. From the corrected volume used calculate the value of the solution in terms of metallic silver and its relation to a normal solution. Repeat until the results are concordant.

> *Notes.*—1. The crystals of silver nitrate sometimes inclose water, which is expelled on drying. If the nitrate has come into contact with organic bodies it suffers a reduction and blackens during the heating.
>
> 2. It is plain that a standard solution of silver nitrate (made by weighing out the crystals) is convenient or necessary if many titrations of this nature are to be made. In the absence of such a solution the liability of passing the endpoint is lessened by setting aside a small fraction of the silver solution, to be added at the close of the titration.

DETERMINATION OF SILVER IN COIN

Procedure.—Weigh out two portions of the coin of about 0.5 gram each. Dissolve them in 15 cc. of nitric acid (sp. gr. 1.2) and boil until all the nitrous compounds are expelled; cool the liquid, dilute to 50 cc., add 5 cc. of the indicator solution, and titrate with the thiocyanate to the appearance of the faint red coloration.

From the corrected volume of the thiocyanate solution

required, calculate the weight of silver present and the percentage in the coin.

Note.—The solution containing the silver precipitate, as well as those from the standardization, should be placed in the receptacle for "silver residues."

PART IV

STOICHIOMETRY

THE stoichiometrical problems with which the analytical chemist has to deal are not, as a rule, difficult either to solve or to comprehend. The student will find that a moderate time devoted to the thoughtful study of these problems will do much to prevent embarrassment in later professional experience, where the ability to make the necessary calculations for the interpretation of analytical data is no less important than the manipulative skill by which the data are obtained.

Detailed solutions of a few typical problems are given below. The student should study these carefully, and assure himself that they are fully understood.

1. A " chemical factor " expresses the ratio between a specific quantity of an element or chemical compound and the *equivalent* quantity of some other body. For example, if it is wished to determine the weight of sulphur which corresponds to a specific weight of barium sulphate, the latter is multiplied by the factor, or ratio, represented by the fraction $\dfrac{S}{BaSO_4}$, or $\dfrac{32.06}{233.46} = 0.1373$. It may also be expressed by the proportion $BaSO_4 : S =$ wt. $BaSO_4 : x$, from which it is plain that $x = \dfrac{32.06}{233.46}$ wt. $BaSO_4$.

Again, if the weight of FeO in Fe_2O_3 is desired, the factor becomes $\dfrac{2FeO}{Fe_2O_3} = \dfrac{143.8}{159.8} = 0.9001$. Similarly, the factor for the conversion of KCl to K_2O is $\dfrac{K_2O}{2KCl} = \dfrac{94.3}{149.2} = 0.6320$. The logarithmic equivalents of these values are called log factors.

In the calculation of these factors, the atomic or molecular relations of the two substances must be kept clearly in mind; thus it is plainly *incorrect* to express the ratio of ferrous to ferric oxide by the fraction $\dfrac{FeO}{Fe_2O_3}$, since each molecule of the higher oxide must correspond to two molecules of the lower. Carelessness in this respect is one of the most frequent sources of error.

2. To calculate the volume of a reagent required for a specific operation, it is necessary to know the exact reaction which is to be brought about, and, as with the calculation of factors, to keep in mind the molecular relations between the reagent and the substance reacted upon. For example, to estimate the weight of barium chloride necessary to precipitate the sulphur from 0.1 gram of pure pyrite (FeS_2), the proportion should stand $2\overset{488.6}{\left(BaCl_2.2H_2O\right)}$: $\overset{120.02}{FeS_2} = x : 0.1$, where x represents the weight of the chloride required. Each of the two atoms of sulphur will form upon oxidation a molecule of sulphuric acid or a sulphate, which, in turn, will require a molecule of the barium chloride for precipitation. To determine the quantity of the barium chloride required, it is necessary to include in its molecular weight the water of crystallization, since this is inseparable from the chloride when it is weighed. This applies equally to other similar instances.

If the strength of an acid is expressed in percentage by weight, due regard must be paid to its specific gravity. For example, hydrochloric acid (sp. gr. 1.12) contains 23.8 per cent. HCl *by weight;* that is, 0.2666 gram HCl in each cubic centimeter.

3. No rules of universal application to "indirect gravimetric analyses" can be laid down. The single example explained below represents a common type.

Given a mixture of KCl + NaCl weighing 0.15 gram, which contains 53 per cent. chlorine, to calculate the weight of KCl and of NaCl in the mixture.

The weight of chlorine in the mixture is (0.15 × 0.53) or 0.0795 gram. Assuming that this chlorine was all in combination with potassium, the corresponding weight of KCl would be 0.1672 gram (Cl : KCl = 0.0795 : 0.1672). This is an excess of 0.0172 gram over the actual weight of the mixture, and it is plain that this difference is occasioned by the replacement of certain of the molecules of potassium chloride, weighing 74.6 units, by molecules of sodium chloride weighing 58.50 units. To express this, let it be supposed that the mixture is made up of n molecules KCl and n' molecules NaCl; then it may be said that $n\overset{74.6}{KCl} + n'\overset{58.50}{NaCl} = $ 0.15 gram, and $n\overset{74.6}{KCl} + n'\overset{74.6}{KCl} = $ 0.1672 gram. Subtracting the first equation from the second shows that $n'(\overset{74.6}{KCl} - \overset{58.50}{NaCl}) = $ 0.0172 gram. That is, the difference in weight is equal to n' times the

difference in the molecular weights of the two chlorides. The actual weight of NaCl present (x) is equal to $58.50n'$, or, since $n' = \dfrac{0.0172}{74.6 - 58.50}$, $x = 58.50\left(\dfrac{0.0172}{74.6 - 58.50}\right)$. This may be expressed in the form $(74.6 - 58.50) : 58.50 = 0.0172 : x$, from which $x = 0.0625$. The weight (x) of NaCl subtracted from that of the mixture obviously gives the weight of KCl.

The weights of the chlorides may also be calculated algebraically by solving the equations $x + y = 0.15$ and $\dfrac{35.45}{74.6}x + \dfrac{35.45}{58.50}y = 0.0795$, where x is the weight of KCl and y is the weight of NaCl in the mixture.

It should be noted that slight and even unavoidable variations in the results of analyses of the mixture will involve considerable variations in the percentages of the components, as calculated by these "indirect" methods. They are, therefore, employed chiefly when direct methods are inapplicable. Compare Problem 28.

4. It is sometimes desirable to weigh out such a quantity of substance for analysis by volumetric methods, that the number of cubic centimeters of standard solution used shall represent directly the percentage of the desired constituent. This may be readily done by considering the relation of the standard solution to a normal solution (page 75) and the atomic or molecular weight of the component which it is desired to determine. For example, suppose it is desired to calculate such a weight for K_2CO_3 in pearlash, when a half-normal acid solution is used. Since half-normal acid and alkali solutions are equivalent, and since, by definition, the half-normal K_2CO_3 solution contains 34.57 grams per liter, each cubic centimeter of the acid solution must be equivalent to 0.03457 gram K_2CO_3. Hence 100 cc. would neutralize 3.457 grams pure K_2CO_3, and this becomes the desired weight of the pearlash, since each cubic centimeter then corresponds to 1 per cent. of the material under analysis. Similarly, the required weight of limonite, where the iron (Fe) is to be determined by means of a deci-normal $K_2Cr_2O_7$ solution, is 0.5590 gram.

5. One of the most frequently recurring cases in volumetric analysis is that in which it is wished to express the value of a specific solution in terms of some substance other than that against

which it has been standardized; as, for instance, the value of a permanganate solution which has been standardized against oxalic acid, in terms of iron. Such problems at first appear to differ widely among themselves, but are, in fact, dependent upon very simple principles of *equivalence*. These are illustrated here, and if once thoroughly understood, as it is essential that they should be, this class of problems presents no further difficulty.

Suppose, for example, it is desired to find the iron value (Fe) of a potassium permanganate solution, of which 1 cc. is equivalent to 0.0063 gram $C_2H_2O_4.2H_2O$.
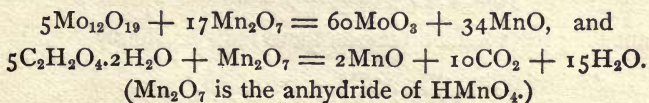
From a comparison of the reactions on page 115, it is seen that 10 molecules of ferrous sulphate and 5 molecules of oxalic acid each react with the same amount (2 molecules) of the permanganate. These two quantities being, then, equivalent to the same third quantity must be equivalent to each other; in other words, 10 molecules of ferrous sulphate and 5 molecules of oxalic acid have the same reducing power. But, as stated above, the value is desired in terms of metallic iron (Fe), not $FeSO_4$; but as it is plain that $10FeSO_4$ are equivalent to $10Fe$, it is proper to make the proportion

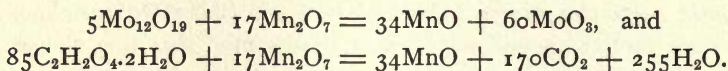$$10\overset{559}{Fe} : 5\left(C_2H_2\overset{630}{O_4}.2H_2O\right) = x : 0.0063$$

in which $x = 0.00559$ gram. Here, again, as in example 2, it is necessary to include the water of crystallization in the molecular weight of the oxalic acid, as it is weighed with it.

The same conclusion is arrived at, if we consider the relation of the solution to the normal. As given, it is deci-normal and must, therefore, be equivalent to a deci-normal solution of iron. From the equations cited it is seen that $10FeSO_4$ unite with $5O$, therefore each molecule of $FeSO_4$ is equivalent to 1 hydrogen atom in reducing power. The normal solution must, then, contain 1 gram-molecule of ferrous sulphate, or 55.9 grams Fe, and each cubic centimeter of the deci-normal solution would contain 0.00559 gram, the value obtained above.

Again, suppose the value of the same permanganate solution were desired in terms of molybdenum (Mo), the reactions with the permanganate being

$$5Mo_{12}O_{19} + 17Mn_2O_7 = 60MoO_3 + 34MnO, \quad \text{and}$$
$$5C_2H_2O_4.2H_2O + Mn_2O_7 = 2MnO + 10CO_2 + 15H_2O.$$
$$\text{(Mn_2O_7 is the anhydride of $HMnO_4$.)}$$

It is plain that in these equations as they stand the molecular quantities of oxidizing agent are not equal. They can be made so by simply multiplying the second equation by 17, and they then become,

$$5Mo_{12}O_{19} + 17Mn_2O_7 = 34MnO + 60MoO_3, \text{ and}$$
$$85C_2H_2O_4.2H_2O + 17Mn_2O_7 = 34MnO + 170CO_2 + 255H_2O.$$

It is now possible to reason in the same way as before, and to conclude that 85 molecules of the oxalic acid have the same reducing power as 5 molecules of the oxide $Mo_{12}O_{19}$, or 60 atoms of molybdenum. Accordingly,

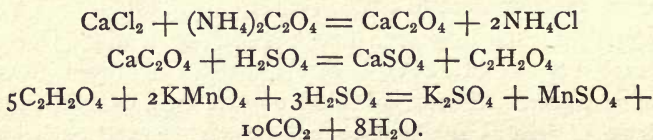$$60\overset{5760}{Mo} : 85\left(C_2H_2\overset{10710}{O_4}.2H_2O\right) = x : 0.0063$$

in which $x = 0.003388$ gram.

Since $5Mo_{12}O_{19}$ unite with 85O, a normal solution of the former as a reducing agent would contain $\frac{1}{170}$ of the 5 gram-molecules or 33.88 grams Mo, and the deci-normal solution 3.388 grams per liter. This agrees with the values already obtained.

6. It is sometimes necessary to calculate the value of solutions according to the principles just explained, when several successive reactions are involved. Such problems may be solved by a series of proportions, but it is usually possible to eliminate the common factors and solve but a single one.

For example, suppose it is desired to express the value of a permanganate solution, of which 1 cc. = 0.008 gram iron (Fe), in terms of calcium oxide (CaO). The reactions involved in the volumetric determination of calcium are the following:

$$CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl$$
$$CaC_2O_4 + H_2SO_4 = CaSO_4 + C_2H_2O_4$$
$$5C_2H_2O_4 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + MnSO_4 + 10CO_2 + 8H_2O.$$

From the considerations stated under 5 the following proportions may be made:

$$10Fe : 5C_2H_2O_4.2H_2O = .008 : x$$
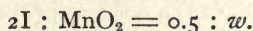$$5C_2H_2O_4.2H_2O : 5CaC_2O_4 = x : y$$
$$5CaC_2O_4 : 5CaO = y : z.$$

Canceling the common factors, there remains simply

$$10\overset{559}{Fe} : 5\overset{280.5}{CaO} = .008 : z.$$

Similarly, from the reactions given in Note 6, page 125, the equivalent of the iodine liberated may be calculated in terms of MnO_2 as follows: Supposing the weight of iodine to be 0.5 gram, then

$$2I : 2KI = 0.5 : x$$
$$2KI : 2Cl = x : y$$
$$2Cl : 2HCl = y : z$$
$$2HCl : MnO_2 = z : w.$$

Canceling the common factors, there remains

$$2I : MnO_2 = 0.5 : w.$$
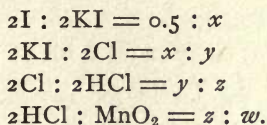
To solve such problems as 5 and 6, it is necessary to know the reactions involved, and also to understand the *nature* of the changes which the individual components undergo; then to compare the reactions and to search for those molecular quantities of the compounds in question which are *equivalent* in their action upon a common agent. Having found these, as shown above, express the molecular ratio between them in the form of a proportion; as, for example, $2\overset{254}{I} : \overset{87}{MnO_2} = 0.5 : w$. Expressed in the form $w = \dfrac{87}{254}\, 0.5$, it is plain that this ratio is in no way different in principle from the chemical factor mentioned in paragraph 1; indeed, it is the factor for the conversion of iodine to manganese dioxide.

PROBLEMS

(The reactions necessary for the solution of these problems are either stated with the problem or may be found in the earlier text. In the calculations from which the answers are derived, the atomic weights given on page 166 (1908) have been employed, using, however, only the first decimal, but increasing this by 1 when the second decimal is 5 or above. Thus, 39.2 has been taken as the atomic weight of potassium, 32.1 for sulphur, etc. This has been done merely to secure uniformity of treatment, and the student should remember that it is always well to take into account the degree of accuracy desired in a particular instance in determining the number of decimal places to retain. Four-place logarithms were employed in the calculations. Where four figures are given in the answer the last figure may vary by one or (rarely) by two units, according to the method by which the problem is solved.)

GRAVIMETRIC ANALYSIS

1. Calculate the chemical factors for (a) $(NH_4)_2O$ from $(NH_4)_2PtCl_6$; (b) for K in K_2PtCl_6; (c) for P in $Mg_2P_2O_7$; (d) for Fe_2O_3 from Fe_3O_4.
Answers: (a) 0.1171; (b) 0.1613; (c) 0.2783; (d) 1.035.

2. Calculate the log factor for (a) As_2O_3 from $Mg_2As_2O_7$; (b) Mn_2O_3 from Mn_3O_4; (c) for Sb in Sb_2O_4; (d) ZnO in $ZnNH_4PO_4.2H_2O$.
Answers: (a) 9.8042-10; (b) 0.0149; (c) 9.8974-10; (d) 9.5794-10.

3. If 0.5 gram of platinum remains after the ignition of the precipitate of the double salt, $(NH_4)_2PtCl_6$, derived from 1 gram of an ammonium compound, calculate the percentage of NH_3 in the latter. $(NH_4)_2PtCl_6 = 2NH_3 + 2HCl + 2Cl_2 + Pt$.
Answer: 8.73%.

4. What weight of Mn_3O_4 corresponds to 1 gram of $Mn_2P_2O_7$?
Answer: 0.5376 gram.

5. What weight of $BaSO_4$ will be obtained by the addition of barium chloride to a solution containing 0.5 gram of ferric alum $[Fe(NH_4)(SO_4)_2.12H_2O]$?
Answer: 0.4844 gram.

6. How many cubic centimeters of aqueous ammonia (sp. gr. 0.96, containing 9.97% NH_3 by weight) will be required to precipitate the iron as $Fe(OH)_3$ from 1 gram of $(NH_4)_2SO_4.FeSO_4.6H_2O$?
Answer: 1.36 cc.

7. How many cubic centimeters of HNO_3 (sp. gr. 1.135, containing 20% HNO_3 by weight) are required to oxidize the iron in 1 gram of $FeSO_4.(NH_4)_2SO_4.6H_2O$ in the presence of sulphuric acid? $6FeSO_4 + 2HNO_3 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$.
Answer: 0.24 cc.

8. A sample of alum $[KAl(SO_4)_2.12H_2O]$ weighing 0.6 gram is dissolved in water, and 10 cc. of hydrochloric acid (sp. gr. 1.12, containing 23.8% HCl by weight) are added. How many cubic centimeters of aqueous ammonia (sp. gr. 0.90, containing 28.4% NH_3 by weight) are required to neutralize the acid and precipitate the aluminium hydroxide from this solution? *Answer:* 5.11 cc.

9. How many cubic centimeters of bromine water, containing 30 grams of bromine per liter, are required to oxidize the iron

in 2 grams of $FeSO_4.7H_2O$ in the presence of sulphuric acid?
$$2FeSO_4.7H_2O + H_2SO_4 + Br_2 = Fe_2(SO_4)_3 + 2HBr + 7H_2O.$$
Answer: 19.19 cc.

10. The ignited precipitate of $Fe_2O_3 + Al_2O_3$ from 1.5 grams of a silicate weighs 0.4069 gram; this mixture loses 0.0200 gram on ignition in hydrogen, the ferric oxide alone being reduced. What is the percentage of Fe_2O_3 and Al_2O_3 in the sample? $Fe_2O_3 + 3H_2 = 2Fe + 3H_2O.$

Answers: 4.44% Fe_2O_3; 22.69% Al_2O_3.

11. A sample of slaked lime [$Ca(OH)_2$ and $CaCO_3$] weighing 0.6 gram is treated with concentrated sulphuric acid, and the residue, after ignition, is found to weigh 0.8743 gram. Find the total percentage of CaO in the sample. $Ca(OH)_2 + CaCO_3 + 2H_2SO_4 = 2CaSO_4 + CO_2 + 3H_2O.$ *Answer:* 60.02%.

12. A sample of pyrite weighing 0.5 gram yields 1.6 grams $BaSO_4$. Calculate the percentage FeS_2 in the sample.

Answer: 82.28%.

13. A sample of magnetite weighing 0.6 gram, after solution and oxidation and precipitation of the iron, yields 0.62 gram of Fe_2O_3. To what percentage of Fe_3O_4 does this correspond?

Answer: 99.88%.

14. How many cubic centimeters of "magnesia mixture" (64 grams $MgCl_2$ per liter) will be required to precipitate the arsenic from 0.2 gram As_2S_3 after oxidation to arsenic acid? $H_3AsO_4 + MgCl_2 + 3NH_4OH = MgNH_4AsO_4 + 2NH_4Cl + 3H_2O.$ *Answer:* 2.42 cc.

15. How many cubic centimeters of an ammonium oxalate solution [$(NH_4)_2C_2O_4.H_2O$, 40 grams per liter] are required to precipitate the calcium as oxalate from 1 gram of apatite [$Ca_3(PO_4)_2.CaCl_2$]? How many cubic centimeters of "magnesia mixture" (containing 64 grams $MgCl_2$ per liter) are necessary to combine with the phosphoric acid in the same weight of apatite?

Answers: 33.69 cc. and 7.07 cc.

16. If a calcium oxalate precipitate (which is contaminated by silica) from 0.83 gram of dolomite be ignited under such conditions that the decomposition products may be passed through $Ba(OH)_2$ solution, and the resulting precipitate of $BaCO_3$ be found on drying to weigh 0.9500 gram, what is the percentage of CaO in the sample? *Answer:* 32.53%.

17. How many cubic centimeters of a solution of sodium hydrogen phosphate, containing 100 grams of $NaH_2PO_4.12H_2O$ per liter, are required to precipitate the zinc as $ZnNH_4PO_4$ from a sample of brass if the ignited precipitate in the form of $Zn_2P_2O_7$ weighs 0.3850 gram? *Answer:* 8.49 cc.

18. It is desired to prepare a solution of potassium dichromate ($K_2Cr_2O_7$) of such a strength that after reduction of the chromium to chromium sulphate (in the presence of sulphuric acid) 50 cc. will yield 0.75 gram Cr_2O_3 after precipitation by ammonia and ignition of the precipitate. How many grams per liter of $K_2Cr_2O_7$ must the solution contain? $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$ *Answer:* 29.03 grams.

19. How many cubic centimeters of a potassium acid oxalate solution (KHC_2O_4), containing 25 grams per liter, would be required to precipitate the calcium from 1 gram of a sample of dolomite yielding, beside a small insoluble residue, 2% Fe_2O_3, 10% MgO, and 45% CO_2, assuming iron, magnesium, and calcium to be present wholly as carbonates, the iron as ferrous carbonate? *Answer:* 38.47 cc.

20. How many cubic centimeters of sulphuric acid (sp. gr. 1.75), containing 81% H_2SO_4 by weight, are necessary to replace the nitric acid in the nitrates formed from 5 grams of a brass containing 65% Cu, 34.5% Zn, and 0.5% Pb? *Answer:* 5.37 cc.

21. If 5.23 grams of brass yield 0.0345 gram $PbSO_4$, and subsequently 0.0031 gram PbO_2 on electrolysis of one-fifth of the filtrate, what is the percentage of Pb in the brass? *Answer:* 0.71%.

22. If in the analysis of a brass containing 65% copper an error is made in weighing a 2.5-gram portion by which 0.001 gram too much is weighed out, what would be the percentage of copper as determined? If the same error is made in weighing 0.2 gram of apatite containing 40% P_2O_5, what will be the apparent percentage? What will be the percentage error in each case? *Answers:* 65.03%; 40.20%; 0.04%; 0.50%.

23. If in the analysis of a given substance a variation of 0.1% is allowable, and if it is found desirable to use 15 grams for analysis, how accurately is it necessary to weigh the sample? *Answer·* To 15 milligrams.

24. A sample of iron ore contains 45% Fe, and 5 grams are weighed out for analysis. If the iron is precipitated from one-tenth of the solution, how large an error in the weight of the precipitate of Fe_2O_3 must be made in order to produce an error amounting to 0.1% of the apparent amount of Fe in the ore?

Answer: 0.0003 gram.

25. If 1.5 grams of glass yield 0.38 gram KCl + NaCl, from which 0.646 gram K_2PtCl_6 is obtained, what is the percentage of Na_2O in the glass? *Answer:* 6.42%.

26. A mixture of BaO and CaO weighing 0.2438 gram yields 0.4876 gram of mixed sulphates. What is the weight of each oxide in the original mixture?

Answers: CaO, 0.1287 gram; BaO, 0.1151 gram.

27. From the following data calculate the per cent. of each of the salts present in the mixture of sodium chloride, bromide, and iodide: Weight of the mixture taken for analysis, 0.75 gram. Weight of the silver iodide obtained after distilling off the iodine and precipitation with silver nitrate, 0.5281 gram. Weight of AgCl + AgBr obtained from solution after removal of iodine, 0.8922 gram. Weight of this precipitate after conversion of the AgBr into AgCl by treatment with chlorine, 0.8113 gram.

Answers: 45% NaI; 25% NaBr; 30% NaCl.

28. In duplicate analyses of a mixture of anhydrous sodium and potassium sulphates the weights of barium sulphate obtained from 0.5 gram of the mixture were 0.7826 and 0.7815 gram. Find the variation in percentage of SO_4 in the mixture as thus determined, and also the variation in the percentage of anhydrous sodium sulphate in the mixture as calculated separately from each of the weights of barium sulphate obtained.

Answers: 0.07% and 0.72%.

29. Calculate the percentage of pure Na_2CO_3 in an impure sample from the following data: Crucible + SiO_2 = 20.0697 grams; crucible + SiO_2 + Na_2CO_3 (impure) = 20.3264 grams; crucible + SiO_2 (excess) + Na_2SiO_3 (after fusion) = 20.2239 grams. Assume the reaction to be $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$. *Answer:* 96.36%.

30. In the course of the analysis of a nitrogenous substance, of which 0.5 gram was weighed out, there is obtained 64 cc. of

nitrogen gas, measured over water at $17°$ C. and 770 mm. pressure. What is the percentage of nitrogen in the substance? (The pressure of aqueous vapor at $17°$ C. is 14 mm.; 1 liter of nitrogen under standard conditions weighs 1.257 grams.)

Answer: 15.07%.

VOLUMETRIC ANALYSIS

31. How much crude cream of tartar should be taken for an analysis in order that the number of cubic centimeters of $\frac{N}{2}$ NaOH solution required to react with it shall represent directly the percentage of $KHC_4H_4O_6$? How much oxalic acid in order that each cubic centimeter of $\frac{N}{10}$ $KMnO_4$ may represent 1% $C_2H_2O_4.2H_2O$? $KHC_4H_4O_6 + NaOH = KNaC_4H_4O_6 + H_2O$.

Answers: 9.41 grams and 0.63 gram.

32. If 10.62 grams of soda ash are dissolved in water and the solution diluted to 1000 cc., and 250 cc. of this solution is taken for titration, what should be the strength of the standard acid solution in order that the burette reading may indicate directly the percentage of Na_2CO_3 in the soda·ash?

Answer: $\frac{N}{2}$.

33. What weight of potassium ferrocyanide, $K_4Fe(CN)_6.3H_2O$, should a $\frac{N}{5}$ solution contain · for use as a reducing agent? $10K_4Fe(CN)_6.(3H_2O) + 2KMnO_4 + 8H_2SO_4 = 10K_3Fe(CN)_6 + 6K_2SO_4 + 2MnSO_4 + 8H_2O + (30H_2O)$.

Answer: 84.54 grams per liter.

34. Calculate the weight of $KHC_2O_4.C_2H_2O_4.(2H_2O)$ necessary for a liter of normal solution, (*a*) as a standard acid solution (compare note on page 97), (*b*) as a reducing agent. $KHC_2O_4.C_2H_2O_4.(2H_2O) + 2MnO_2 + 3H_2SO_4 = 2MnSO_4 + KHSO_4 + 4CO_2 + 6H_2O$.

Answers: (*a*) 84.73 grams and (*b*) 63.55 grams.

35. What weight of stannous chloride ($SnCl_2$) is required for a $\frac{N}{10}$ solution for use as a reducing agent? $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$.

Answer: 9.5 grams per liter.

36. If 10 cc. of a sulphuric acid solution yield 0.1220 gram $BaSO_4$, how much must the solution be diluted to become an exactly $\frac{N}{10}$ solution?

Answer: 1000 cc. to 1045 cc.

37. If 1 cc. of potassium bichromate solution will oxidize 0.0066 gram iron, to what volume must 100 cc. of the solution be diluted to make a $\dfrac{N}{100}$ solution? *Answer:* 1180 cc.

38. A solution of potassium permanganate, of which 1 cc. will react with 0.03056 gram of ferrous sulphate ($FeSO_4.7H_2O$), has been diluted to 1200 cc. with the intention of preparing a $\dfrac{N}{10}$ solution. How much too large is the volume?

Answer: 100 cc.

39. If a liter of dilute nitric acid will exactly neutralize 5.75 grams of $HNaCO_3$, how much water must be added to 1000 cc. of the acid to make a $\dfrac{N}{5}$ solution as an oxidizing agent? $2HNO_3 = 2NO + H_2O + 3O$. *Answer:* 25.5 cc.

40. Calculate the percentage of carbon dioxide (CO_2) in a sample of calcium carbonate from the following data: Total volume $\dfrac{N}{2}$ $HCl = 35$ cc.; total volume $\dfrac{N}{10}$ $NaOH = 15$ cc.; weight carbonate $= 1.00$ gram. *Answer:* 35.20%.

41. Given the following data, calculate the percentage purity of the oxalic acid:
Standardization: Weight $CaCO_3 = 1.050$ grams; HCl solution used $= 45$ cc.; NaOH solution used $= 4.8$ cc.; 1 cc. NaOH solution $= 1.042$ cc. HCl solution.
Analysis: Weight of oxalic acid $= 1.500$ grams; NaOH solution used $= 42.5$ cc.; HCl solution used $= 0.5$ cc.

Answer: 96.42%.

42. Given the following data, calculate the percentage purity of the cream of tartar ($KHC_4H_4O_6$):
Weight of substance $= 2.500$ grams; NaOH solution used $= 25.51$ cc.; H_2SO_4 solution used $= 0.5$ cc.; 1 cc. of H_2SO_4 solution $= 1.02$ cc. NaOH solution; 1 cc. NaOH solution $= 0.0255$ gram $CaCO_3$. *Answer:* 95.90%.

43. If 1500 cc. of a solution contain 25 grams of NaOH and 14 grams of KOH, what is the relation of this solution to a normal alkali solution? *Answer:* 0.5819.

44. Calculate the percentage of K_2CO_3 in a sample of pearlash from the following data:

Weight of sample $= 6.4$ grams; HCl used for one-fourth of solution 48 cc.; NaOH used $= 6$ cc.; 1 cc. HCl $= 0.02501$ gram $CaCO_3$; NaOH solution is $\dfrac{N}{3}$.　　　*Answer: 95.10%.*

45.　Solutions of alkali carbonates with phenolphthalëin become colorless as soon as the carbonate has changed to bicarbonate. Calculate the percentage NaOH in a sample of soda ash from the following data, assuming the hydrate to be neutralized before the carbonate is attacked: Weight of soda ash $= 1$ gram; HCl solution is $\dfrac{N}{2}$. The solution becomes colorless when 25 cc. HCl have been added, but requires 40 cc. for complete neutralization after boiling out the carbon dioxide. $Na_2CO_3 + HCl = HNaCO_3 + NaCl$; $NaHCO_3 + HCl = NaCl + CO_2 + H_2O$.

Answer: 20.05%.

46.　Calculate the percentage of iron (Fe) in a sample of limonite from the following data:

Weight of limonite $= 0.55$ gram; $K_2Cr_2O_7$ solution used $= 51.1$ cc.; 1 cc. $K_2Cr_2O_7$ solution $= .0058$ gram Fe; $FeSO_4$ solution used $= 5$ cc.; 5 cc. of $FeSO_4$ solution contains 0.008 gram FeO.　　*Answer: 52.76%.*

47.　A sample of iron wire is dissolved, out of contact with air, in 30 cc. HCl, of which 1 cc. $= 0.95$ cc. $\dfrac{N}{2}$ HCl. The iron requires 40 cc. $\dfrac{N}{10}$ $K_2Cr_2O_7$ for oxidation. What excess of HCl was used over that actually required for solution?

Answer: 13.16 cc.

48.　How much stannous chloride ($SnCl_2$) by weight will it require to reduce the iron from 0.5 gram magnetite ($FeO.Fe_2O_3$) dissolved out of contact with air?　*Answer: 0.4101 gram.*

49.　How many cubic centimeters of HCl (sp. gr. 1.12) actually combine with the ferric oxide from 0.55 gram of limonite ($2Fe_2O_3.3H_2O$), assuming the only impurity to be 1.5% quartz.

Answer: 2.38 cc.

50.　If 0.75 gram of a silicate yields 0.4 gram $Fe_2O_3 + Al_2O_3$, and the iron present required 20 cc. $K_2Cr_2O_7$ solution (1 cc. $= 0.0784$ gram $FeSO_4(NH_4)_2SO_4.6H_2O$), calculate the percentage of FeO and Al_2O_3 in the sample.

Answers: 38.32% and 10.72%.

51. What weight of iron wire containing 99.85% Fe will, when dissolved in acid, exactly react with the chromium from 0.5 gram chromite ($FeO.Cr_2O_3$)? *Answer:* 0.7496 gram.

52. What is the maximum weight of a mixed iron ore containing 10% magnetite ($FeO.Fe_2O_3$) and 20% limonite ($2Fe_2O_3.3H_2O$) which can be taken for analysis without requiring a refilling of a 50 cc. burette, provided the total iron is to be determined, and a 0.125N solution of $K_2Cr_2O_7$ is employed for titration?
Answer: 1.819 grams.

53. If in the analysis of a sample of chromite weighing 0.52 gram a piece of scale (from the iron crucible) weighing .005 gram falls into the acidified solution of the fusion and is dissolved, how and to what extent is the apparent percentage of Cr_2O_3 in error? (Assume the composition of the scale to be $FeO.Fe_2O_3$.)
Answer: 0.11% too low.

54. If 1 cc. of a potassium permanganate solution will oxidize 0.0085 gram Fe, calculate the value of the same solution in terms of (*a*) $KHC_2O_4.C_2H_2O_4.2H_2O$; (*b*) KNO_2; (*c*) Mn; (*d*) $K_4Fe(CN)_6.3H_2O$.
$10KHC_2O_4.C_2H_2O_4.(2H_2O) + 8KMnO_4 + 17H_2SO_4 = 9K_2SO_4 + 8MnSO_4 + 40CO_2 + 32H_2O + (20H_2O)$; $10KNO_2 + 4KMnO_4 + 11H_2SO_4 = 7K_2SO_4 + 4MnSO_4 + 10HNO_3 + 6H_2O$; $3MnO + Mn_2O_7 = 5MnO_2$, and $2KMnO_4 = K_2O.Mn_2O_7$. Compare also Problem 2.
Answers: (*a*) 0.009663; (*b*) 0.006477; (*c*) 0.002509; (*d*) 0.06427 gram.

55. Calculate the value of a permanganate solution, of which 1 cc. = 0.008 gram Fe, in terms of MoO_3. $Mn_2O_7 + 10FeO = 5Fe_2O_3 + 2MnO$; $7Mn_2O_7 + Mo_{24}O_{37} = 24MoO_3 + 14MnO$.
Answer: 0.007066 gram.

56. Given the following data, calculate the percentage of iron in the limonite:
Weight of the limonite = 0.55 gram; $KMnO_4$ solution used = 30 cc.; 1 cc. $KMnO_4$ solution = 0.0084 gram $C_2H_2O_4.2H_2O$.
Answer: 40.65%.

57. The calcium oxalate precipitate from 0.5 gram marble, when treated with sulphuric acid, liberates sufficient oxalic acid

to reduce 43 cc. of permanganate solution (1 cc. = 0.01150 gram Fe). Calculate the percentage of calcium (Ca) in the marble.

Answer: 35.47%.

58. If 1 cc. of $KMnO_4$ solution will oxidize 0.008 gram iron (Fe), calculate the equivalent of the same solution in terms of hydrogen dioxide (H_2O_2), and also the volume of oxygen which will be evolved on the addition of each cubic centimeter of the permanganate solution during the reaction, assuming that 1 cc. of oxygen weighs 0.00143 gram. $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$

Answers: 0.002433 gram; 1.6 cc.

59. If 1 cc. of a solution of hydrogen dioxide (sp. gr. 1.01) when brought into contact with potassium permanganate yields 10 cc. of oxygen gas, what per cent. by weight of H_2O_2 does it contain? (See Problem 58.)   *Answer:* 1.5%.

60. In the analysis of an iron ore 0.35 gram is taken, and 40 cc. of a $\dfrac{N}{10}$ $KMnO_4$ solution are used in the titration; but sulphurous acid was used to reduce the iron and an amount equivalent to 0.005 gram SO_2 remained in the solution after boiling. What error is introduced into the determination of the iron (Fe) in the ore, and what is the correct percentage?

Answers: 2.49% and 61.39%.

61. Given the following data, calculate the percentage of MnO_2 in the pyrolusite:

Weight of the pyrolusite = 0.48 gram; weight of $FeSO_4$. $(NH_4)_2SO_4.6H_2O$ = 4.3501 grams; $K_2Cr_2O_7$ solution used = 10 cc.; 1 cc. $K_2Cr_2O_7$ solution = 0.005 gram Fe. *Answer:* 92.45%.

62. Given the following data, calculate the percentage of MnO_2 in the pyrolusite:

Weight of pyrolusite = 0.48 gram; weight of iodine liberated from KI = 1.296 grams.

For reactions, see Note 6, page 125.   *Answer:* 92.51%.

63. What weight of pyrolusite containing 85% MnO_2 will oxidize the same amount of oxalic acid as 45 cc. of a $KMnO_4$ solution of which 1 cc. will liberate 0.0190 gram iodine from potassium iodide? $2KMnO_4 + 10KI + 8H_2SO_4 = 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O.$ *Answer:* 0.3445 gram.

64. If 1 cc. iodine solution is equivalent in oxidizing power to 0.00149 gram $KBrO_3$, to what volume must 100 cc. be diluted to make a $\dfrac{N}{20}$ solution?   *Answer:* 106.9 cc.

65.   Calculate the percentage purity of a sample of potassium bichromate from the following data:

Weight of sample = 0.1232 gram; $Na_2S_2O_3$ solution used = 25 cc.; 1 cc. $Na_2S_2O_3$ solution = 1.004 cc. iodine solution; 1 cc. iodine solution = 0.00495 gram As_2O_3. $K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O.$

Answer: 100%.

66.   Given the following data:

30 cc. $K_2Cr_2O_7$ solution = 45 cc. $Na_2S_2O_3$ solution (for equation, see Problem 65); 50 cc. $K_2Cr_2O_7$ solution = 0.2795 gram Fe. 15 cc. iodine solution = 20 cc. $Na_2S_2O_3$ solution. Find the relation of the iodine solution to a normal solution.

Answer: 0.0889N.

67.   Calculate the percentage purity of a sample of potassium iodate (KIO_3) from the following data:

Weight of sample = 0.25 gram; $Na_2S_2O_3$ solution used = 50 cc.; 1 cc. $Na_2S_2O_3$ solution = 0.015 gram I.   *Answer:* 84.35%.

68.   If 1 cc. of an iodine solution has the same oxidizing power as 0.0034 gram KIO_3, calculate the value in terms of antimony (Sb).   *Answer:* 0.005724 gram.

69.   A mixture of the chlorides of sodium and potassium from 0.5 gram of a feldspar weighs 0.15 gram, and after solution in water requires 22.71 cc. of $\dfrac{N}{10}$ $AgNO_3$ for the precipitation of the chloride ions. What are the percentages of Na_2O and K_2O in the feldspar?   *Answers:* 7.58% and 9.93%.

70.   What is the relation of each of the following solutions to a normal solution of the reagent?

(*a*) $Na_2S_2O_3.5H_2O$: 1 cc. = 0.001784 gram KIO_3.
(*b*) $KMnO_4$ (acid solution): 1 cc. = 0.0063 gram $C_2H_2O_4.2H_2O$.
(*c*) As_2O_3 (as a reducing agent): 1 cc. = 0.01772 gram Cl.
(*d*) As_2O_3 (as an acid): 1 cc. = 0.01061 gram Na_2CO_3.
(*e*) NaOH: 1 cc. = 0.1694 gram $KHC_2O_4.C_2H_2O_4.2H_2O$.

Answers: (*a*) 0.04997N; (*b*) 0.1N; (*c*) 0.4992N; (*d*) 0.1998N; (*e*) 2N.

APPENDIX

ELECTROLYTIC DISSOCIATION THEORY

THE following brief statements concerning the ionic theory and a few of its applications are intended for reference in connection with the explanations which are given in the Notes accompanying the various procedures. The reader who desires a more extended discussion of the fundamental theory and its uses is referred to such books as Talbot and Blanchard's *Electrolytic Dissociation Theory* (Macmillan Company), or Alexander Smith's *Introduction to General Inorganic Chemistry* (Century Company).

The *electrolytic dissociation theory*, as propounded by Arrhenius in 1887, assumes that acids, bases, and salts (that is, electrolytes) in aqueous solution are dissociated to a greater or less extent into *ions*. These ions are assumed to be electrically charged atoms or groups of atoms, as, for example, H^+ and Br^- from hydrobromic acid, Na^+ and OH^- from sodium hydroxide, $2NH_4^+$ and SO_4^{--} from ammonium sulphate. The unit charge is that which is associated with a hydrogen ion. Those upon other ions vary in sign and number according to the chemical character and valence of the atoms or radicals of which the ions are composed. In any solution the aggregate of the positive charges upon the positive ions (*cations*) must always balance the aggregate negative charges upon the negative ions (*anions*).

It is assumed that the Na^+-ion, for example, differs from the sodium atom in behavior because of the very considerable electrical charge which it carries and which, as just stated, must, in an electrically neutral solution, be balanced by a corresponding negative charge on some other ion. When an electric current is passed through a solution of an electrolyte the ions move with and convey the current, and when the cations come into contact with the negatively charged cathode they lose their charges, and the resulting electrically neutral atoms (or radicals) are liberated as such, or else enter at once into chemical reaction with the components of the solution.

Two ions of identically the same composition but with different

electrical charges may exhibit widely different properties. For example, the ion MnO_4^- from permanganates yields a purple-red solution and differs in its chemical behavior from the ion MnO_4^{--} from manganates, the solutions of which are green.

The chemical changes upon which the procedures of analytical chemistry depend are almost exclusively those in which the reacting substances are electrolytes, and analytical chemistry is, therefore, essentially the chemistry of the ions.

The percentage dissociation of the same electrolyte tends to increase with increasing dilution of its solution, although not in direct proportion. The percentage dissociation of different electrolytes in solutions of equivalent concentrations (such, for example, as normal solutions) varies widely, as is indicated in the following tables, in which approximate figures are given for deci-normal solutions at a temperature about 18° C. To facilitate comparisons, the percentages given for the polybasic acids are based on the assumption that, so far as they are ionized at all, they yield simultaneously their maximum number of H^+-ions; thus, $H_3PO_4 \rightarrow 3H^+ + PO_4^{---}$.

ACIDS

Substance.	Percentage dissociation in 0.1 equivalent solution.
HCl, HBr, HI, HNO$_3$, HClO$_3$, HClO$_4$, HMnO$_4$	90
H_2SO_4	60
$H_2C_2O_4$	34
H_2SO_3	20
H_3PO_4	13
H_3AsO_4	11
HF	9
$HC_2H_3O_2$	1.4
H_2CO_3	0.12
H_2S	0.05
HCN	0.01

BASES

Substance.	Percentage dissociation in 0.1 equivalent solution.
KOH, NaOH	86
Ba(OH)$_2$	75
NH$_4$OH	1.4

SALTS

Type of salt.	Percentage dissociation in 0.1 equivalent solution.
R^+R^-	86
$R^{++}(R^-)_2$	72
$(R^+)_2R^{--}$	72
$R^{++}R^{--}$	45

The percentage dissociation is determined by studying the electrical conductivity of the solutions and by other physico-chemical methods, and the following general statements summarize the results:

Salts, as a class, are largely dissociated in aqueous solution.

Acids yield H^+-ions in water solution, and the comparative *strength*, that is, the activity, of acids is proportional to the concentration of the H^+-ions and is measured by the percentage dissociation in solutions of equivalent concentration. The common mineral acids are largely dissociated and therefore give a relatively high concentration of H^+-ions, and are commonly known as "strong acids." The organic acids, on the other hand, belong generally to the group of "weak acids."

Bases yield OH^--ions in water solution, and the comparative strength of the bases is measured by their relative dissociation in solutions of equivalent concentration. Ammonium hydroxide is a weak base, as shown in the table above, while the hydroxides of sodium and potassium exhibit strongly basic properties.

Ionic reactions are all, to a greater or less degree, *reversible reactions*. A typical example of an easily reversible reaction is that representing the changes in ionization which an electrolyte such as acetic acid undergoes on dilution or concentration of its

solutions, namely, $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$. As was stated above, the ionization increases with dilution, the reaction then proceeding from left to right, while concentration of the solution occasions a partial reassociation of the ions, and the reaction proceeds from right to left. To understand the principle underlying these changes it is necessary to consider first the conditions which prevail when a solution of acetic acid, which has been stirred until it is of uniform concentration throughout, has come to a constant temperature. A careful study of such solutions has shown that there is a definite state of equilibrium between the constituents of the solution; that is, there is a definite relation between the undissociated acetic acid and its ions, which is characteristic for the prevailing conditions. It is not, however, assumed that this is a condition of static equilibrium, but rather that there is continual dissociation and association, as represented by the opposing reactions, the apparent condition of rest resulting from the fact that the amount of change in one direction during a given time is exactly equal to that in the opposite direction. A quantitative study of the amount of undissociated acid, and of H^+-ions and $C_2H_3O_2^-$-ions actually to be found in a large number of solutions of acetic acid of varying dilution (assuming them to be in a condition of equilibrium at a common temperature), has shown that there is always a definite relation between these three quantities which may be expressed thus:

$$\frac{Conc'n\ H^+ \times Conc'n\ C_2H_3O_2^-}{Conc'n\ HC_2H_3O_2} = Constant.$$

In other words, there is always a definite and constant ratio between the product of the concentrations of the ions and the concentration of the undissociated acid when conditions of equilibrium prevail.

It has been found, further, that a similar statement may be made regarding all reversible reactions, which may be expressed in general terms thus: The rate of chemical change is proportional to the product of the concentrations of the substances taking part in the reaction; or, if conditions of equilibrium are considered in which, as stated, the rate of change in opposite directions is assumed to be equal, then the product of the concentrations of the substances entering into the reaction stands in a constant ratio to the product of the concentrations of the

resulting substances, as given in the expression above for the
solutions of acetic acid. This principle is called the *Law of
Mass Action.*

It should be borne in mind that the expression above for acetic
acid applies to a wide range of dilutions, provided the tempera-
ture remains constant. If the temperature changes the value of
the constant changes somewhat, but is again uniform for different
dilutions at that temperature. The following data are given for
temperatures about 18° C.[1]

Molal concentration.	Fraction ionized.	Molal concentration of H+ and $C_2H_3O_2{}^-$-ions.	Molal concentration of undissociated acid.	Value of constant.
1.0	.004	.004	.996	.0000161
0.1	.013	.0013	.0987	.0000171
0.01	.0407	.000407	.009593	.0000172

The molal concentrations given in the table refer to fractions
of a gram-molecule per liter of the undissociated acid, and to
fractions of the corresponding quantities of H+ and $C_2H_3O_2{}^-$-ions
per liter which would result from the complete dissociation of
a gram-molecule of acetic acid. The values calculated for the
constant are subject to some variation on account of experimental
errors in determining the percentage ionized in each case, but
the approximate agreement between the values found for molal
and centimolal solutions (one hundredfold dilution) is significant.

The figures given also illustrate the general principle, that the
relative ionization of an electrolyte increases with the dilution
of its solution. If we consider what happens during the (usually)
brief period of dilution of the solution from molal to 0.1 molal,
for example, it will be seen that on the addition of water the
conditions of concentration which led to equality in the rate of
change, and hence to equilibrium in the molal solution, cease to
exist; and since the dissociating tendency increases with dilution,
as just stated, it is true at the first instant after the addition of
water that the concentration of the undissociated acid is too great
to be permanent under the new conditions of dilution, and the
reaction, $HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2{}^-$, will proceed from left to

[1] Alexander Smith, *General Inorganic Chemistry,* p. 579.

right with great rapidity until the respective concentrations adjust themselves to the new conditions.

That which is true of this reaction is also true of all reversible reactions, namely, that any change of conditions which occasions an increase or a decrease in concentration of one or more of the components causes the reaction to proceed in one direction or the other until a new state of equilibrium is established. This principle is constantly applied throughout the discussion of the applications of the ionic theory in analytical chemistry, and it should be clearly understood that whenever an existing state of equilibrium is disturbed as a result of changes of dilution or temperature, or as a consequence of chemical changes which bring into action any of the constituents of the solution, thus altering their concentrations, there is always a tendency to reëstablish this equilibrium in accordance with the law. Thus, if a base is added to the solution of acetic acid the H^+-ions then unite with the OH^--ions from the base to form undissociated water. The concentration of the H^+-ions is thus diminished, and more of the acid dissociates in an attempt to restore equilibrium, until finally practically all the acid is dissociated and neutralized.

Similar conditions prevail when, for example, silver ions react with chloride ions, or barium ions react with sulphate ions. In the former case the dissociation reaction of the silver nitrate is $AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$, and as soon as the Ag^+-ions unite with the Cl^--ions the concentration of the former is diminished, more of the $AgNO_3$ dissociates, and this process goes on until the Ag^+-ions are practically all removed from the solution, if the Cl^--ions are present in sufficient quantity.

For the sake of accuracy it should be stated that the mass law cannot be rigidly applied to solutions of those electrolytes which are largely dissociated. While the explanation of the deviation from quantitative exactness in these cases is not known, the law is still of marked service in developing analytical methods along more logical lines than was formerly practicable. It has not seemed wise to qualify each statement made in the Notes to indicate this lack of quantitative exactness. The student should recognize its existence, however, and will realize its significance better as his knowledge of physical chemistry increases.

If we apply the mass law to the case of a substance of small solubility, such as the compounds usually precipitated in quan-

titative analysis, we derive what is known as the *solubility product,* as follows: Taking silver chloride as an example, and remembering that it is not absolutely insoluble in water, the equilibrium expression for its solution is:

$$\frac{Conc'n\ Ag^+ \times Conc'n\ Cl^-}{Conc'n\ AgCl} = Constant.$$

But such a solution of silver chloride which is in contact with the solid precipitate must be saturated for the existing temperature, and the quantity of undissociated AgCl in the solution is definite and practically constant for that temperature. Since it is a constant it may be eliminated, and the expression becomes *Conc'n Ag⁺ × Conc'n Cl⁻ = Constant,* and this is known as the solubility product. No precipitation of a specific substance will occur until the product of the concentrations of its ions in a solution exceeds the solubility product for that substance; whenever that product is exceeded precipitation must follow.

It will be readily seen that if a substance which yields an ion in common with the precipitated compound is added to such a solution as has just been described, the concentration of that ion is increased, and as a result the concentration of the other ion must proportionately decrease, which can only occur through the formation of some of the undissociated compound which must separate from the already saturated solution. This explains why the addition of an excess of the precipitant is often advantageous in quantitative procedures. Such a case is discussed at length in Note 1 on page 32.

Similarly the ionization of a specific substance in solution tends to diminish on the addition of another substance with a common ion, as, for instance, the addition of hydrochloric acid to a solution of hydrogen sulphide. Hydrogen sulphide is a weak acid, and the concentration of the hydrogen ions in its aqueous solutions is very small. The equilibrium in such a solution may be represented as:

$$\frac{(Conc'n\ H^+)^2 \times Conc'n\ S^{--}}{Conc'n\ H_2S} = Constant,$$

and a marked increase in the concentration of the H⁺-ions, such as would result from the addition of even a small amount of the

highly ionized hydrochloric acid, displaces the point of equilibrium and some of the S⁻⁻-ions unite with H⁺-ions to form undissociated H_2S. This is of much importance in studying the reactions in which hydrogen sulphide is employed, as in qualitative analysis. By a parallel course of reasoning it will be seen that the addition of a salt of a weak acid or base to solutions of that acid or base make it, in effect, still weaker because they decrease its percentage ionization.

To understand the changes which occur when solids are dissolved where chemical action is involved, it should be remembered that no substance is completely insoluble in water, and that those products of a chemical change which are least dissociated will first form. Consider, for example, the action of hydrochloric acid upon magnesium hydroxide. The dissolved hydroxide dissociates thus: $Mg(OH)_2 \rightleftharpoons Mg^{++} + 2OH^-$. When the acid is introduced, the H⁺-ions of the acid unite with the OH⁻-ions to form undissociated water. The concentration of the OH⁻-ions is thus diminished, more $Mg(OH)_2$ dissociates, the solution is no longer saturated with the undissociated compound, and more of the solid dissolves. This process repeats itself with great rapidity until, if sufficient acid is present, the solid passes completely into solution.

Exactly the same sort of process takes place if calcium oxalate, for example, is dissolved in hydrochloric acid. The $C_2O_4^{--}$-ions unite with the H⁺-ions to form undissociated oxalic acid, the acid being less dissociated than normally in the presence of the H⁺-ions from the hydrochloric acid (see statements regarding hydrogen sulphide above). As the undissociated oxalic acid forms, the concentration of the $C_2O_4^{--}$-ions lessens and more CaC_2O_4 dissolves, as described for the $Mg(OH)_2$ above. Numerous instances of the applications of these principles are given in the Notes.

Water itself is slightly dissociated, and although the resulting H⁺ and OH⁻-ions are present only in minute concentrations (1 mol of dissociated water in 10⁷ liters), yet under some conditions they may give rise to important consequences. The term *hydrolysis* is applied to the changes which result from the reaction of these ions. Any salt which is derived from a weak base or a weak acid (or both) is subject to hydrolytic action. Potassium cyanide, for example, when dissolved in water gives an alkaline

solution because some of the H^+-ions from the water unite with CN^--ions to form (HCN), which is a very weak acid, and is but very slightly dissociated. Potassium hydroxide, which might form from the OH^--ions, is so largely dissociated that the OH^--ions remain as such in the solution. The union of the H^+-ions with the CN^--ions to form the undissociated HCN diminishes the concentration of the H^+-ions, and more water dissociates $(H_2O \rightleftharpoons H^+ + OH^-)$ to restore the equilibrium. It is clear, however, that there must be a gradual accumulation of OH^--ions in the solution as a result of these changes, causing the solution to exhibit an alkaline reaction, and also that ultimately the further dissociation of the water will be checked by the presence of these ions, just as the dissociation of the H_2S was lessened by the addition of HCl.

An exactly opposite result follows the solution of such a salt as $Al_2(SO_4)_3$ in water. In this case the acid is strong and the base weak, and the OH^--ions form the little dissociated $Al(OH)_3$, while the H^+-ions remain as such in the solution, sulphuric acid being extensively dissociated.

Such hydrolytic processes as the above are of great importance in analytical chemistry, especially in the understanding of the action of indicators in volumetric analysis. (See page 88.)

The impelling force which causes an element to pass from the atomic to the ionic condition is termed *electrolytic solution pressure,* or ionization tension. This force may be measured in terms of electrical potential, and the table on the following page shows the relative values for a number of elements.

In general, an element with a greater solution pressure tends to cause the deposition of an element of less solution pressure when placed in a solution of its salt, as, for instance, when a strip of zinc or iron is placed in a solution of a copper salt, with the resulting precipitation of metallic copper.

Hydrogen is included in the table, and its position should be noted with reference to the Notes on pages 63 and 64. For a more extended discussion of this topic the student should refer to other treatises.

POTENTIAL SERIES OF THE METALS [1]

	Potential in volts.		Potential in volts.
Sodium . . . . Na$^+$	. .	Lead . . . . . Pb^{++}	—0.129
Calcium . . . . Ca^{++}	. .	Hydrogen . . . H$^+$	—0.277
Magnesium . . . Mg^{++}	. .	Bismuth . . . . Bi^{+++}	. .
Aluminium . . . Al^{+++}	. .	Antimony	. .
Manganese . . . Mn^{++}	. .	Arsenic	. .
Zinc . . . . . . Zn^{++}	+0.493	Copper . . . . Cu^{++}	—0.606
Cadmium . . . Cd^{++}	+0.143	Mercury . . . . Hg$^+$	—1.027
Iron . . . . . . Fe^{++}	+0.063	Silver . . . . . Ag$^+$	—1.048
Cobalt . . . . . Co^{++}	—0.045	Palladium . . . Pd^{++}	. .
Nickel . . . . . Ni^{++}	—0.049	Platinum	. .
Tin . . . . . . Sn^{++}	—0.085(?)	Gold	. .

[1] From Talbot and Blanchard, *Electrolytic Dissociation Theory.*

TABLE OF ATOMIC WEIGHTS

$$O = 16.00$$

	(1908)[1]		(1908)
Aluminium . . . . . . Al	27.1	Molybdenum . . . . . Mo	96.0
Antimony . . . . . . Sb	120.2	Neodymium . . . . . Nd	143.6
Argon . . . . A	39.9	Neon . . . . Ne	20.
Arsenic . . . . As	75.0	Nickel . . . . Ni	58.7
Barium . . . . Ba	137.4	Nitrogen . . . . . . N	14.01
Bismuth . . . . Bi	208.0	Osmium . . . . Os	191.2
Boron . . . . B	11.0	Oxygen . . . . O	16.00
Bromine . . . . Br	79.96	Palladium . . . . . . Pd	106.5
Cadmium . . . . . . Cd	112.4	Phosphorus . . . . . P	31.0
Cæsium . . . . Cs	132.9	Platinum . . . . . . Pt	194.8
Calcium . . . . Ca	40.1	Potassium . . . . . . K	39.15
Carbon C	12.00	Praseodymium . . . . Pr	140.5
Cerium . . . . Ce	140.25	Radium . . . . Rd	225.
Chlorine Cl	35.45	Rhodium . . . . . . Rh	103.0
Chromium . . . . . . Cr	52.1	Rubidium . . . . . . Rb	85.5
Cobalt . . . . Co	59.0	Ruthenium . . . . . Ru	101.7
Columbium . . . . . Cb	94.	Samarium . . . . . . Sm	150.3
Copper . . . . Cu	63.6	Scandium . . . . . . Sc	44.1
Dysprosium . . . . . Dy	162.5	Selenium . . . . . . Se	79.2
Erbium . . . . Er	166.	Silicon . . . . Si	28.4
Europium . . . . . . Eu	152.	Silver . . . . Ag	107.93
Fluorine . . . . Fl	19.0	Sodium . . . . Na	23.05
Gadolinium . . . . . Gd	156.	Strontium . . . . . . Sr	87.6
Gallium . . . . Ga	70.0	Sulphur . . . . S	32.06
Germanium . . . . . Ge	72.5	Tantalum . . . . . . Ta	181.
Glucinum . . . . . . Gl	9.1	Tellurium . . . . . . Te	127.6
Gold . . . . Au	197.2	Terbium . . . . Tb	159.2
Helium . . . . He	4.0	Thallium . . . . . . Tl	204.1
Hydrogen . . . . . . H	1.008	Thorium . . . . . . Th	232.5
Indium . . . . In	115.	Thulium . . . . . . Tm	171.
Iodine I	126.97	Tin . . . . Sn	119.0
Iridium . . . . Ir	193.0	Titanium . . . . . . Ti	48.1
Iron . . . . Fe	55.9	Tungsten . . . . . . W	184.0
Krypton . . . . Kr	81.8	Uranium . . . . . . U	238.5
Lanthanum . . . . . La	138.9	Vanadium V	51.2
Lead . . . . Pb	206.9	Xenon . . . . Xe	128.
Lithium Li	7.03	Ytterbium . . . . . . Yb	173.0
Magnesium . . . . . Mg	24.36	Yttrium . . . . Y	89.0
Manganese . . . . . Mn	55.0	Zinc . . . . Zn	65.4
Mercury . . . . Hg	200.0	Zirconium . . . . . . Zr	90.6

[1] International Committee on Atomic Weights, *J. Am. Chem. Soc.*, **30** (1908), 1.

STRENGTH OF REAGENTS

The concentrations given in this table are those suggested for use in the procedures described in the foregoing pages. It is obvious, however, that an exact adherence to these quantities is not essential.

	Grams per liter.	Approx. relation to normal solution.	Approx. relation to molal solution.
Ammonium molybdate [1] (of MoO_3) . .	68	N	0.5
Ammonium oxalate, $(NH_4)_2C_2O_4.H_2O$.	40	$\frac{N}{2}$	0.25
Barium chloride, $BaCl_2.2H_2O$ . . .	25	$\frac{N}{5}$	0.1
Magnesium ammonium chloride (of $MgCl_2$),	71	1.5N	0.75
Mercuric chloride, $HgCl_2$	45	$\frac{N}{3}$	0.66
Potassium hydroxide, KOH (sp. gr. 1.27) .	480		
Potassium thiocyanate, KSCN . . .	5	$\frac{N}{20}$	0.05
Silver nitrate, $AgNO_3$	21	$\frac{N}{8}$	0.125
Sodium hydroxide, NaOH . . .	100	2.5N	2.5
Sodium carbonate, Na_2CO_3 . . .	159	3N	1.5
Sodium phosphate, $HNa_2PO_4.12H_2O$.	90	$\frac{N}{2}$ or $\frac{3N}{4}$	0.25

Stannous chloride, $SnCl_2$, made by saturating hydrochloric acid (sp. gr. 1.2) with tin, diluting with an equal volume of water, and adding a slight excess of acid from time to time. A strip of metallic tin is kept in the bottle.

The following data regarding the common acids and aqueous ammonia are based upon percentages given in the Standard Tables of the Manufacturing Chemists' Association of the United States [*J. S. C. I.*, 24 (1905), 787–790]. All gravities are taken at 15.5° C. and compared with water at the same temperature.

Aqueous ammonia (sp. gr. 0.96) contains 9.91 per cent. NH_3 by weight, and corresponds to a 5.6 N and 5.6 molal solution.

Aqueous ammonia (sp. gr. 0.90) contains 28.52 per cent. NH_3 by weight, and corresponds to a 15.1 N and 15.1 molal solution.

Hydrochloric acid (sp. gr. 1.12) contains 23.81 per cent. HCl by weight, and corresponds to a 7.3 N and 7.3 molal solution.

Hydrochloric acid (sp. gr. 1.20) contains 39.80 per cent. HCl by weight, and corresponds to a 13.1 N and 13.1 molal solution.

[1] This solution is prepared according to the formula of Blair and Whitfield, *J. Am. Chem. Soc.*, 17, 760.

Nitric acid (sp. gr. 1.20) contains 32.25 per cent. HNO_3 by weight, and corresponds to a 6.1 N acid and 6.1 molal solution.

Nitric acid (sp. gr. 1.42) contains 69.96 per cent. HNO_3 by weight, and corresponds to a 15.8 N acid and 15.8 molal solution.

Sulphuric acid (sp. gr. 1.8354) contains 93.19 per cent. H_2SO_4 by weight, and corresponds to a 34.8 N or 17.4 molal solution.

Sulphuric acid (sp. gr. 1.18) contains 24.74 per cent. H_2SO_4 by weight, and corresponds to a 5.9 N or 2.95 molal solution.

The term "normal" (N), as used above, has the same significance as in volumetric analyses. It may also be noted that it is the same as the "equivalent" used by Reddrop in his system of equivalent reagents described in *Chem. News,* **61** (1890), 245 and 256. The molal solution is assumed to contain one molecular weight in grams in a liter of solution.

DENSITIES AND VOLUMES OF WATER AT TEMPERATURES FROM 15–30° C.

Temperature Centigrade.	Density.	Volume.
4°	1.000000	1.000000
15°	0.999126	1.000874
16°	0.998970	1.001031
17°	0.998801	1.001200
18°	0.998622	1.001380
19°	0.998432	1.001571
20°	0.998230	1.001773
21°	0.998019	1.001985
22°	0.997797	1.002208
23°	0.997565	1.002441
24°	0.997323	1.002685
25°	0.997071	1.002938
26°	0.996810	1.003201
27°	0.996539	1.003473
28°	0.996259	1.003755
29°	0.995971	1.004046
30°	0.995673	1.004346

Authority: Landolt, Börnstein, and Meyerhoffer's *Tabellen*, third edition.

CORRECTIONS FOR CHANGE OF TEMPERATURE OF STANDARD SOLUTIONS

The values below are average values computed from data relating to a considerable number of solutions. They are sufficiently accurate for use in chemical analyses, except in the comparatively few cases where the highest attainable accuracy is demanded in chemical investigations. The expansion coefficients should then be carefully determined for the solutions employed. For a compilation of the existing data, consult Landolt, Börnstein, and Meyerhoffer's *Tabellen,* third edition.

Concentration.	Corrections for 1 cc. of solution between 15° and 25° C.
Normal	.00029
0.5 Normal	.00025
0.1 Normal or more dilute solutions	.00020

The volume of solution used should be multiplied by the values given, and that product multiplied by the number of degrees which the temperature of the solution varies from the standard temperature selected for the laboratory. The total correction thus found is subtracted from the observed burette reading if the temperature is higher than the standard, or added, if it is lower. Corrections are not usually necessary for variations of temperature of 2° C. or less.

Natural numbers	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

LOGARITHMS OF NUMBERS

Natural numbers.	0	1	2	3	4	5	6	7	8	9	Proportional Parts.								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	4
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	978	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Loga-rithms.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
											PROPORTIONAL PARTS.								
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	3	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

Logarithms.	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
															PROPORTIONAL PARTS.				
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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