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Chemical Analysis, by Henry P. Talbot

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With Explanatory Notes

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\*\*\* START OF THIS PROJECT GUTENBERG EBOOK QUANTITATIVE CHEMICAL ANALYSIS \*\*\*

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[Transcriber's notes: In the chemical equations, superscripts are

indicated with a ^ and subscripts are indicated with a \_. The affected

item is enclosed in curly brackets {}. Examples are H^{+} for hydrogen

ion and H\_{2}O for water. Since the underscore is already being used

in this project, italics are designated by an exclamation point

before and after the italicized word or phrase.]

AN INTRODUCTORY COURSE

OF

QUANTITATIVE

CHEMICAL ANALYSIS

WITH

EXPLANATORY NOTES

BY

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TECHNOLOGY

SIXTH EDITION, COMPLETELY REWRITTEN

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 larger works. The general directions are intended to emphasize

those matters upon which the beginner in quantitative analysis must

bestow special care, and to offer 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 first

course of quantitative analysis at the Massachusetts Institute of

Technology, and have been chosen, after an experience of 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 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.

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; no considerable credit is claimed by him

for originality of procedure.

For many years, as a matter of convenience, the classes for which this

text was originally prepared were divided, one part beginning with

gravimetric processes and the other with volumetric analyses. After a

careful review of the experience thus gained the conclusion has been

reached that volumetric analysis offers the better approach to the

subject. Accordingly the arrangement of the present (the sixth)

edition of this manual has been changed to introduce volumetric

procedures first. Teachers who are familiar with earlier editions

will, however, find that the order of presentation of the material

under the various divisions is nearly the same as that previously

followed, and those who may still prefer to begin the course of

instruction with gravimetric processes will, it is believed, be able

to follow that order without difficulty.

Procedures for the determination of sulphur in insoluble sulphates,

for the determination of copper in copper ores by iodometric methods,

for the determination of iron by permanganate in hydrochloric acid

solutions, and for the standardization of potassium permanganate

solutions using sodium oxalate as a standard, and of thiosulphate

solutions using copper as a standard, have been added. The

determination of silica in silicates decomposable by acids, as a

separate procedure, has been omitted.

The explanatory notes have been rearranged to bring them into closer

association with the procedures to which they relate. The number of

problems has been considerably increased.

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. He is under special obligations

to Professor L.F. Hamilton for assistance in the preparation of the

present edition.

HENRY P. TALBOT

!Massachusetts Institute of Technology, September, 1921!.

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PART I

INTRODUCTION

SUBDIVISIONS OF ANALYTICAL CHEMISTRY

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!.

A preliminary 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 will 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 frequently the same as those employed in

qualitative analyses with respect to both precipitation and systematic

separation from interfering substances; 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 separation 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 take into account 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 analysis, volumetric

analysis!, and !colorimetric analysis!. In !gravimetric! processes the

constituent to be determined is sometimes isolated in elementary

form, but more commonly in the form of some compound possessing a

well-established and definite composition, which can be readily and

completely separated, and weighed either directly or after ignition.

From the weight of this substance and its known 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 from an apparatus so designed that the volume of the

solution employed to complete the reaction can be accurately measured.

The strength of this solution (and hence its value for the reaction

in question) is accurately known, and the volume employed serves,

therefore, as a measure of the substance acted upon. An example will

make clear the distinction between these two types of analysis.

The percentage of chlorine in a sample of sodium chloride may be

determined by dissolving a weighed amount of the chloride in water

and precipitating the chloride ions as silver chloride, which is

then 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 from

a measuring device called a burette 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, require less apparatus,

and are frequently capable of greater accuracy than gravimetric

methods. They are particularly useful when many determinations of the

same sort are required.

In !colorimetric! analyses the substance to be determined is converted

into some compound which imparts to its solutions a distinct color,

the intensity of which must vary in direct proportion to the amount of

the compound in the solution. Such solutions are compared with respect

to depth of color with standard solutions containing known amounts of

the colored compound, or of other similar color-producing substance

which has been found acceptable as a color standard. Colorimetric

methods are, in general, restricted to the determinations of very

small quantities, since only in dilute solutions are accurate

comparisons of color possible.

GENERAL DIRECTIONS

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. The suggestions here given

are the outcome of much experience, and their adoption will tend to

insure permanently work of a high grade, while neglect of them will

often lead to disappointment and loss of time.

ACCURACY AND ECONOMY OF TIME

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. 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. All filters and

solutions should be covered to protect them from dust, just as far as

is practicable, and every drop of solution or particle of precipitate

must be regarded as invaluable for the success of the analysis.

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 !entire! procedure, but the explanatory notes as well, before

any step is taken in the analysis. The explanatory notes furnish, in

general, the reasons for particular steps or precautions, but they

also occasionally contain details of manipulation not incorporated,

for various reasons, in the procedure. These notes follow the

procedures at frequent intervals, and the exact points to which they

apply are indicated by references. The student should realize that a

!failure to study the notes will inevitably lead to mistakes, loss of

time, and an inadequate understanding of the subject!.

All analyses should be made in duplicate, and in general a close

agreement of 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 of their accuracy 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.

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 in manipulation can possibly be.

NOTEBOOKS

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. Several sample pages of systematic

records are to be found in the Appendix. These are based upon

experience; but other arrangements, if clear and orderly, may prove

equally serviceable. The student is advised to follow the sample pages

until he is in a position to plan out a system of his own.

REAGENTS

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 may be others who share the responsibility for the purity

of materials in the laboratory of an institution, the responsibility

will later be one which he must individually assume.

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.

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.

TRANSFER OF LIQUIDS

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 other means to prevent the loss of

liquid by running down the side; whenever loss seems imminent a !very

thin! layer of vaseline, applied with the finger to the edge of the

vessel, will prevent it. 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 or lip of a vessel.

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.

All stirring rods employed in quantitative analyses should be rounded

at the ends by holding them in the flame of a burner until they begin

to soften. If this is not done, the rods will scratch the inner

surface of beakers, causing them to crack on subsequent heating.

EVAPORATION OF LIQUIDS

The greatest care must 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.

PART II

VOLUMETRIC ANALYSIS

The processes of volumetric analysis are, in general, simpler than

those of gravimetric analysis and accordingly serve best as an

introduction to the practice of quantitative analysis. For their

execution there are required, first, an accurate balance with which

to weigh the material for analysis; second, graduated instruments in

which to measure the volume of the solutions employed; third, standard

solutions, that is, solutions the value of which is accurately known;

and fourth, indicators, which will furnish accurate evidence of the

point at which the desired reaction is completed. The nature of the

indicators employed will be explained 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 volume of the standard solution

used then furnishes the measure of the substance to be determined as

truly as if that substance had been separated and weighed.

The processes of volumetric analysis are easily classified, according

to their character, into:

I. NEUTRALIZATION 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 in each case may

be subdivided into (a) DIRECT METHODS, in which the substance to be

measured is directly determined by titration to an end-point with a

standard solution; 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.

MEASURING INSTRUMENTS

THE ANALYTICAL BALANCE

For a complete discussion of the physical principles underlying the

construction and use of balances, and the various methods of weighing,

the student is referred to larger manuals of Quantitative Analysis,

such as those of Fresenius, or Treadwell-Hall, and particularly to

the admirable discussion of this topic in Morse's !Exercises in

Quantitative Chemistry!.

The statements and rules of procedure which follow are sufficient

for the intelligent use of an analytical balance in connection with

processes prescribed in this introductory manual. It is, however,

imperative that the student should make himself familiar with these

essential features of the balance, and its use. He should fully

realize that the analytical balance is a delicate instrument which

will render excellent service under careful treatment, but such

treatment is an essential condition if its accuracy is to be depended

upon. He should also understand that no set of rules, however

complete, can do away with the necessity for a sense of personal

responsibility, since by carelessness he can render inaccurate not

only his own analyses, but those of all other students using the same

balance.

Before making any weighings the student should seat himself before a

balance and observe the following details of construction:

1. The balance case is mounted on three brass legs, which should

preferably rest in glass cups, backed with rubber to prevent slipping.

The front legs are adjustable as to height and are used to level the

balance case; the rear leg is of permanent length.

2. The front of the case may be raised to give access to the balance.

In some makes doors are provided also at the ends of the balance case.

3. The balance beam is mounted upon an upright in the center of the

case on the top of which is an inlaid agate plate. To the center of

the beam there is attached a steel or agate knife-edge on which the

beam oscillates when it rests on the agate plate.

4. The balance beam, extending to the right and left, is graduated

along its upper edge, usually on both sides, and has at its

extremities two agate or steel knife-edges from which are suspended

stirrups. Each of these stirrups has an agate plate which, when the

balance is in action, rests upon the corresponding knife-edge of the

beam. The balance pans are suspended from the stirrups.

5. A pointer is attached to the center of the beam, and as the beam

oscillates this pointer moves in front of a scale near the base of the

post.

6. At the base of the post, usually in the rear, is a spirit-level.

7. Within the upright is a mechanism, controlled by a knob at the

front of the balance case, which is so arranged as to raise the entire

beam slightly above the level at which the knife-edges are in contact

with the agate plates. When the balance is not in use the beam must

be supported by this device since, otherwise, the constant jarring

to which a balance is inevitably subjected, will soon dull the

knife-edges, and lessen the sensitiveness of the balance.

8. A small weight, or bob, is attached to the pointer (or sometimes

to the beam) by which the center of gravity of the beam and its

attachments may be regulated. The center of gravity must lie very

slightly below the level of the agate plates to secure the desired

sensitiveness of the balance. This is provided for when the balance is

set up and very rarely requires alteration. The student should never

attempt to change this adjustment.

9. Below the balance pans are two pan-arrests operated by a button

from the front of the case. These arrests exert a very slight upward

pressure upon the pans and minimize the displacement of the beam when

objects or weights are being placed upon the pans.

10. A movable rod, operated from one end of the balance case, extends

over the balance beam and carries a small wire weight, called a rider.

By means of this rod the rider can be placed upon any desired division

of the scale on the balance beam. Each numbered division on the beam

corresponds to one milligram, and the use of the rider obviates the

placing of very small fractional weights on the balance pan.

If a new rider is purchased, or an old one replaced, care must be

taken that its weight corresponds to the graduations on the beam of

the balance on which it is to be used. The weight of the rider in

milligrams must be equal to the number of large divisions (5, 6, 10,

or 12) between the central knife-edge and the knife-edge at the end of

the beam. It should be noted that on some balances the last division

bears no number. Each new rider should be tested against a 5 or

10-milligram weight.

In some of the most recent forms of the balance a chain device

replaces the smaller weights and the use of the rider as just

described.

Before using a balance, it is always best to test its adjustment. This

is absolutely necessary if the balance is used by several workers; it

is always a wise precaution under any conditions. For this purpose,

brush off the balance pans with a soft camel's hair brush. Then note

(1) whether the balance is level; (2) that the mechanism for raising

and lowering the beams works smoothly; (3) that the pan-arrests touch

the pans when the beam is lowered; and (4) 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 by means of the adjusting

screw at the end of the beam 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.

The object to be weighed should be placed on the left-hand balance pan

and the weights upon the right-hand pan. Every substance which

could attack the metal of the balance pan should be weighed upon a

watch-glass, and all objects must be dry and cold. A warm body gives

rise to air currents which vitiate the accuracy of the weighing.

The weights should be applied in the order in which they occur in the

weight-box (not at haphazard), beginning with the largest weight which

is apparently required. After a weight has been placed upon the pan

the beam should be lowered upon its knife-edges, and, if necessary,

the pan-arrests depressed. The movement of the pointer will then

indicate whether the weight applied is too great or too small. When

the weight has been ascertained, by the successive addition of small

weights, to the nearest 5 or 10 milligrams, the weighing is completed

by the use of the rider. The correct weight is that which causes the

pointer to swing an equal number of divisions to the right and left

of the zero-point, when the pointer traverses not less than five

divisions on either side.

The balance case should always be closed during the final weighing,

while the rider is being used, to protect the pans from the effect 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, in spite of the

pan-arrests, slightly twisted by the impact of the weights, the beam

being thereby virtually lengthened or shortened. Lifting the beam

restores the proper alignment.

The beam should never be set in motion by lowering it forcibly upon

the knife-edges, nor by touching the pans, but rather by lifting 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 approaches 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.

When the process of weighing has been completed, the weight should

be recorded in the notebook by first noting the vacant spaces in the

weight-box, and then checking the weight by again noting the weights

as they are removed from the pan. This practice will often detect and

avoid errors. It is obvious that the weights should always be returned

to their proper places in the box, and be handled only with pincers.

It should be borne in mind that if the mechanism of a balance is

deranged or if any substance is spilled upon the pans or in the

balance case, the damage should be reported at once. In many instances

serious harm can be averted by prompt action when delay might ruin the

balance.

Samples for analysis are commonly weighed in small tubes with cork

stoppers. Since the stoppers are likely to change in weight from

the varying amounts of moisture absorbed from the atmosphere, it is

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.

WEIGHTS

The sets of weights commonly used in analytical chemistry range from

20 grams to 5 milligrams. The weights from 20 grams to 1 gram are

usually of brass, lacquered or gold plated. The fractional weights

are of German silver, gold, platinum or aluminium. The rider is of

platinum or aluminium wire.

The sets of weights purchased from reputable dealers are usually

sufficiently accurate for analytical work. It is not necessary that

such a set should be strictly exact in comparison with the absolute

standard of weight, provided they are relatively correct among

themselves, and provided the same set of weights is used in all

weighings made during a given analysis. The analyst should assure

himself that the weights in a set previously unfamiliar to him are

relatively correct by a few simple tests. For example, he should make

sure that in his set two weights of the same denomination (i.e., two

10-gram weights, or the two 100-milligram weights) are actually equal

and interchangeable, or that the 500-milligram weight is equal to

the sum of the 200, 100, 100, 50, 20, 20 and 10-milligram weights

combined, and so on. If discrepancies of more than a few tenths of a

milligram (depending upon the total weight involved) are found, the

weights should be returned for correction. The rider should also be

compared with a 5 or 10-milligram weight.

In an instructional laboratory appreciable errors should be reported

to the instructor in charge for his consideration.

When the highest accuracy is desired, the weights may be calibrated

and corrections applied. A calibration procedure is described in a

paper by T.W. Richards, !J. Am. Chem. Soc.!, 22, 144, and in many

large text-books.

Weights are inevitably subject to corrosion if not properly protected

at all times, and are liable to damage unless handled with great care.

It is obvious that anything which alters the weight of a single piece

in an analytical set will introduce an error in every weighing made

in which that piece is used. This source of error is often extremely

obscure and difficult to detect. The only safeguard against such

errors is to be found in scrupulous care in handling and protection

on the part of the analyst, and an equal insistence that if several

analysts use the same set of weights, each shall realize his

responsibility for the work of others as well as his own.

BURETTES

A burette is made from a glass tube which is as uniformly cylindrical

as possible, and of such a bore that the divisions which are etched

upon its surface shall correspond closely to actual contents.

The tube is contracted at one extremity, and terminates in either a

glass stopcock and delivery-tube, 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 glass bead. Burettes

of the latter type will be referred to as "plain burettes."

The graduations are usually numbered in cubic centimeters, and the

latter are subdivided into tenths.

One burette of each type is desirable for the analytical procedures

which follow.

PREPARATION OF A BURETTE FOR USE

The inner surface of a burette must be thoroughly cleaned in order

that the liquid as drawn out may drain away completely, without

leaving drops upon the sides. This is best accomplished by treating

the inside of the burette with a warm solution of chromic acid in

concentrated sulphuric acid, applied as follows: If the burette is of

the "plain" type, first remove the rubber tip and force the lower

end of the burette into a medium-sized cork stopper. Nearly fill the

burette with the chromic acid solution, close the upper end with a

cork stopper and tip the burette backward and forward in such a way

as to bring the solution into contact with the entire inner surface.

Remove the stopper and pour the solution into a stock bottle to be

kept for further use, and rinse out the burette with water several

times. Unless the water then runs freely from the burette without

leaving drops adhering to the sides, the process must be repeated

(Note 1).

If the burette has a glass stopcock, this should be removed after

the cleaning and wiped, and also the inside of the ground joint. The

surface of the stopcock should then be smeared with a thin coating of

vaseline and replaced. It should be attached to the burette by means

of a wire, or elastic band, to lessen the danger of breakage.

Fill the burettes with distilled water, and allow the water to run out

through the stopcock or rubber tip until convinced that no air

bubbles are inclosed (Note 2). Fill the burette to a point above the

zero-point and draw off the water until the meniscus is just below

that mark. It is then ready for calibration.

[Note 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. The solution can be prepared by pouring over a

few crystals of potassium bichromate a little water and then adding

concentrated sulphuric acid.]

[Note 2: It is always necessary to insure the absence of air bubbles

in the tips or stopcocks. The treatment described above will usually

accomplish this, but, in the case of plain burettes it is sometimes

better to allow a little of the liquid to flow out of the tip while it

is bent upwards. Any air which may be entrapped then rises with the

liquid and escapes.

If air bubbles escape during subsequent calibration or titration, an

error is introduced which vitiates the results.]

READING OF A BURETTE

All liquids when placed in a burette form what is called a meniscus at

their upper surfaces. In the case of liquids such as water or

aqueous solutions this meniscus is concave, and when the liquids are

transparent accurate readings are best obtained by observing the

position on the graduated scales of the lowest point of the meniscus.

This can best be done as follows: Wrap around the burette a piece of

colored paper, the straight, smooth edges of which are held evenly

together with the colored side next to the burette (Note 1). Hold the

paper about two small divisions below the meniscus and raise or lower

the level of the eyes until the edge of the paper at the back of the

burette is just hidden from the eye by that in front (Note 2). Note

the position of the lowest point of the curve of the meniscus,

estimating the tenths of the small divisions, thus reading its

position to hundredths of a cubic centimeter.

[Note 1: The ends of the colored paper used as an aid to accurate

readings may be fastened together by means of a gummed label. The

paper may then remain on the burette and be ready for immediate use by

sliding it up or down, as required.]

[Note 2: To obtain an accurate reading the eye must be very nearly on

a level with the meniscus. This is secured by the use of the paper

as described. The student should observe by trial how a reading is

affected when the meniscus is viewed from above or below.

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.]

CALIBRATION OF GLASS MEASURING DEVICES

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, or other equally authentic source.

The bore of burettes is subject to accidental variations, and since

the graduations are applied by machine without regard to such

variations of bore, local errors result.

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 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 commonly found in

laboratories, and involves the constant use of corrections if taken as

a laboratory standard. 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 burettes, pipettes, and flasks, should be calibrated at that

temperature in order that the contents of each burette, 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 keep constantly in mind the fact that all

volumetric operations, to be exact, should be carried out 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 THE BURETTES

Two burettes, one at least of which should have a glass stopper, are

required throughout the volumetric work. Both burettes should be

calibrated by the student to whom they are assigned.

PROCEDURE.--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. (See Appendix for

suggestions as to records.) 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) read the burette accurately, and record the reading in the

notebook (Note 1). Meanwhile weigh the flask and water to centigrams

and record its weight (Note 2). 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 cc. is 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 (Note 3).

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, or etching ink, for permanence of record.

[Note 1: 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.]

[Note 2: A comparatively rough balance, capable of weighing to

centigrams, is sufficiently accurate for use in calibrations, for a

moment's reflection will show 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.]

[Note 3: Should the error discovered in any interval of 10 cc. on the

burette exceed 0.10 cc., it is advisable to weigh small 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.

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

tested, this is a more rapid method.]

PIPETTES

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.

Pipettes are usually already graduated when purchased, but they

require calibration for accurate work.

CALIBRATION OF PIPETTES

PROCEDURE.--Clean the pipette. Draw distilled water into it by sucking

at the upper end until the water is well above the graduation mark.

Quickly place the forefinger over the top of the tube, thus preventing

the entrance of air and holding the water in the pipette. Cautiously

admit a little air by releasing the pressure of the finger, and allow

the level of the water to fall until the lowest point of the meniscus

is level with the graduation. Hold the water at that point by pressure

of the finger and then allow the water to run out from the pipette

into a small tared, or weighed, beaker or flask. After a definite time

interval, usually two to three minutes, touch the end of the pipette

against the side of the beaker or flask to remove any liquid adhering

to it (Note 1). The increase in weight of the flask in grams

represents the volume of the water in cubic centimeters delivered by

the pipette. Calculate the necessary correction.

[Note 1: 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, when

adopted, must be uniformly adhered to.]

FLASKS

!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.

GRADUATION OF FLASKS

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. They may be graduated for "contents" or

"delivery." When graduated for "contents" they contain a specified

volume when filled to the graduation at a specified temperature, and

require to be washed out in order to remove all of the solution from

the flask. Flasks graduated for "delivery" will deliver the specified

volume of a liquid without rinsing. A flask may, of course, be

graduated for both contents and delivery by placing two graduation

marks upon it.

PROCEDURE.--To calibrate a flask for !contents!, proceed as follows:

Clean the flask, using a chromic acid solution, and dry it carefully

outside and inside. Tare it accurately; pour water into the flask

until the weight of the latter counterbalances weights on the opposite

pan which equal in grams the number of cubic centimeters of water

which the flask is to contain. Remove any excess of water with the aid

of filter paper (Note 1). 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 (Note 2). The mark may

be etched upon the flask by hydrofluoric acid, or by the use of an

etching ink now commonly sold on the market.

To graduate a flask which is designed to !deliver! a specified volume,

proceed as follows: Clean the flask as usual and wipe all moisture

from the outside. Fill it with distilled water. Pour out the water

and allow the water to drain from the flask for three minutes.

Counterbalance the flask with weights to the nearest centigram.

Add weights corresponding in grams to the volume desired, and add

distilled water to counterbalance these weights. An excess of water,

or water adhering to the neck of the flask, may be removed by means of

a strip of clean filter paper. Stopper the flask, place it in a bath

at 15.5°C. or 17.5°C. and, after an hour, mark the location of the

lowest point of the meniscus, as described above.

[Note 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.]

[Note 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 position of the meniscus marked directly

upon it. For a description of a procedure which is most convenient

when many flasks are to be calibrated, the student is referred to the

!Am. Chem J.!, 16, 479.]

GENERAL DIRECTIONS FOR VOLUMETRIC ANALYSES

It cannot be too strongly emphasized that for the success of analyses

uniformity of practice must prevail throughout all volumetric work

with respect to those factors which can influence the accuracy of the

measurement of liquids. For example, whatever conditions are imposed

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 also be constantly watchful to insure parallel

conditions during both standardization and analyst with respect to the

final volume of liquid in which a titration takes place. The value

of a standard solution is only accurate under the conditions which

prevailed when it was standardized. 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 each to run out through the tip before assuming

that the burette is in a condition to be filled and used. It is, of

course, possible to dry 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 slowly and with accuracy.

In such cases, however, the knowledge of the approximate amount to be

required should never be allowed to influence the judgment regarding

the actual end-point.

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!.

NORMAL SOLUTIONS

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 are

called !Normal Solutions! and contain such an amount of the reacting

substance per liter as is equivalent in its chemical action to one

gram of hydrogen, or eight grams of oxygen. Solutions containing one

half, one tenth, or one one-hundredth of this quantity per liter are

called, respectively, half-normal, tenth-normal, or hundredth-normal

solutions.

Since normal solutions of various reagents are all referred to a

common standard, they have an advantage not possessed by empirical

solutions, namely, that they are exactly equivalent to each other.

Thus, 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 will exactly react with a liter of a normal reducing

solution, and so on.

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

atomic or molecular weight of the constituent to be determined. (See

problem 26.)

The preparation of an !exactly! normal, half-normal, or tenth-normal

solution requires considerable time and care. It 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 solution, 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 some of

the advantage which pertains to the use of normal solutions as regards

simplicity of calculations is lost when using these approximate

solutions.

The application of these general statements will be made clear in

connection with the use of normal solutions in the various types of

volumetric processes which follow.

I. NEUTRALIZATION METHODS

ALKALIMETRY AND ACIDIMETRY

GENERAL DISCUSSION

!Standard Acid Solutions! may be prepared from either hydrochloric,

sulphuric, or oxalic acid. 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 with 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 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, thereby losing

strength; sodium carbonate may be weighed directly if its purity is

assured, but the presence of carbonic acid from 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.

A !normal acid solution! should contain in one liter that quantity of

the reagent which represents 1 gram of hydrogen replaceable by a base.

For example, the normal solution of hydrochloric acid (HCl) should

contain 36.46 grams of gaseous hydrogen chloride, since that amount

furnishes the requisite 1 gram of replaceable hydrogen. On the other

hand, the normal solution of sulphuric acid (H\_{2}SO\_{4}) should

contain only 49.03 grams, i.e., one half of its molecular weight in

grams.

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 (40.01) of sodium hydroxide (NaOH),

while a sodium carbonate solution (Na\_{2}CO\_{3}) should contain but

one half the molecular weight in grams (i.e., 53.0 grams) in a liter

of normal solution.

Half-normal or tenth-normal solutions are employed in most analyses

(except in the case of the less soluble barium hydroxide). Solutions

of the latter strength yield more accurate results when small

percentages of acid or alkali are to be determined.

INDICATORS

It has already been pointed out that the purpose of an indicator is to

mark (usually by a change of color) the point at which just enough of

the titrating solution has been added to complete the chemical change

which it is intended to bring about. In the neutralization processes

which are employed in the measurement of alkalies (!alkalimetry!)

or acids (!acidimetry!) the end-point of the reaction should, in

principle, be that of complete neutrality. Expressed in terms of ionic

reactions, it should be the point at which the H^{+} ions from an

acid[Note 1] unite with a corresponding number of OH^{-} ions from a

base to form water molecules, as in the equation

H^{+}, Cl^{-} + Na^{+}, OH^{-} --> Na^{+}, Cl^{-} + (H\_{2}O).

It is not usually possible to realize this condition of exact

neutrality, but it is possible to approach it with sufficient

exactness for analytical purposes, since substances are known which,

in solution, undergo a sharp change of color as soon as even a minute

excess of H^{+} or OH^{-} ions are present. Some, as will be seen,

react sharply in the presence of H^{+} ions, and others with OH^{-}

ions. These substances employed as indicators are usually organic

compounds of complex structure and are closely allied to the dyestuffs

in character.

[Note 1: A knowledge on the part of the student of the ionic theory

as applied to aqueous solutions of electrolytes is assumed. A brief

outline of the more important applications of the theory is given in

the Appendix.]

BEHAVIOR OF ORGANIC INDICATORS

The indicators in most common use for acid and alkali titrations are

methyl orange, litmus, and phenolphthalein.

In the following discussion of the principles underlying the behavior

of the indicators as a class, methyl orange and phenolphthalein will

be taken as types. It has just been pointed out that indicators are

bodies of complicated structure. In the case of the two indicators

named, the changes which they undergo have 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 is a representative of the group of indicators which,

in aqueous solutions, behave as weak bases. The yellow color which it

imparts to solutions is ascribed to the presence of the undissociated

base. If an acid, such as HCl, is added to such a solution, the acid

reacts with the indicator (neutralizes it) and a salt is formed, as

indicated by the equation:

(M.o.)^{+}, OH^{-} + H^{+}, Cl^{-} --> (M.o.)^{+} Cl^{-} + (H\_{2}O).

This salt ionizes into (M.o.)^{+} (using this abbreviation for the

positive complex) and Cl^{-}; but simultaneously with this ionization

there appears to be an internal rearrangement of the atoms which

results in the production of a cation which may be designated as

(M'.o'.)^{+}, and it is this which imparts a characteristic red color

to the solution. As these changes occur in the presence of even a

very small excess of acid (that is, of H^{+} ions), it serves as the

desired index of their presence in the solution. If, now, an alkali,

such as NaOH, is added to this reddened solution, the reverse

series of changes 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, little-dissociated 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'.)^{+} --> [M'.o'.OH] --> [M.o.OH].

Phenolphthalein, on the other hand, is a very weak, little-dissociated

acid, which is colorless in neutral aqueous solution or in the

presence of free H^{+} ions. When an alkali is added to such a

solution, even in slight excess, the anion of the salt which has

formed from the acid of the indicator undergoes a rearrangement of the

atoms, and a new ion, (Ph')^{+}, is formed, which imparts a pink color

to the solution:

H^{+}, (Ph)^{-} + Na^{+}, OH^{-} --> (H\_{2}O) + Na^{+}, (Ph)^{-}

--> Na^{+}, (Ph')^{-}

The addition of the slightest excess of an acid to this solution, on

the other hand, occasions first the reversion to the colorless ion and

then the setting free of the undissociated acid of the indicator:

H^{+}, (Ph')^{-} --> H^{+}, (Ph)^{-} --> (HPh).

Of the common indicators methyl orange is the most sensitive toward

alkalies and phenolphthalein toward acids; the others occupy

intermediate positions. That methyl orange should be most sensitive

toward alkalies is evident from the following considerations: Methyl

orange is a weak base and, therefore, but little dissociated. It

should, then, be formed in the undissociated condition as soon as even

a slight excess of OH^{-} ions is present in the solution, and there

should be a prompt change from red to yellow as outlined above. On the

other hand, it should be an unsatisfactory indicator for use with weak

acids (acetic acid, for example) because the salts which it forms

with such acids are, like all salts of that type, hydrolyzed to a

considerable extent. This hydrolytic change is illustrated by the

equation:

(M.o.)^{+} C\_{2}H\_{3}O\_{2}^{-} + H^{+}, OH^{-} --> [M.o.OH] + H^{+},

C\_{2}H\_{3}O\_{2}^{-}.

Comparison of this equation with that on page 30 will make it plain

that hydrolysis is just the reverse of neutralization and must,

accordingly, interfere with it. Salts of methyl orange with weak acids

are so far hydrolyzed that the end-point is uncertain, and methyl

orange cannot be used in the titration of such acids, while with

the very weak acids, such as carbonic acid or hydrogen sulphide

(hydrosulphuric acid), the salts formed with methyl orange are, in

effect, completely hydrolyzed (i.e., no neutralization occurs), and

methyl orange is accordingly scarcely affected by these acids. This

explains its usefulness, as referred to later, for the titration of

strong acids, such as hydrochloric acid, even in the presence of

carbonates or sulphides in solution.

Phenolphthalein, on the other hand, should be, as it is, the best of

the common indicators for use with weak acids. For, since it is

itself a weak acid, it is very little dissociated, and its nearly

undissociated, colorless molecules are promptly formed as soon as

there is any free acid (that is, free H^{+} ions) in the solution.

This indicator cannot, however, be successfully used with weak bases,

even ammonium hydroxide; for, since it is weak acid, the salts

which it forms with weak alkalies are easily hydrolyzed, and as a

consequence of this hydrolysis the change of color is not sharp.

This indicator can, however, be successfully used with strong bases,

because the salts which it forms with such bases are much less

hydrolyzed and because the excess of OH^{-} ions from these bases also

diminishes the hydrolytic action of water.

This indicator is affected by even so weak an acid as 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.

In general, it may be stated that 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, since very little

hydrolysis ensues. It has been noted above that the color change does

not occur exactly at theoretical neutrality, from which it follows

that no two indicators will show exactly the same end-point when acids

and alkalis are brought together. It is plain, therefore, that the

same indicator must be employed for both standardization and analysis,

and that, if this is done, accurate results are obtainable.

The following table (Note 1) illustrates the variations in the volume

of an alkali solution (tenth-normal sodium hydroxide) required to

produce an alkaline end-point when run into 10 cc. of tenth-normal

sulphuric acid, diluted with 50 cc. of water, using five drops of each

of the different indicator solutions.

====================================================================

| | | |

INDICATOR | N/10 | N/10 |COLOR IN ACID|COLOR IN ALKA-

| H\_{2}SO\_{4}| NaOH |SOLUTION |LINE SOLUTION

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_

| cc. | 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

Phenolphthalein| 10 | 10.10 | Colorless | Pink

====================================================================

It should also be stated that there are occasionally secondary

changes, other than those outlined above, which depend upon the

temperature and concentration of the solutions in which the indicators

are used. These changes may influence the sensitiveness of an

indicator. 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 of indicator used should be uniform

and not excessive. Usually a few drops of solution will suffice.

The foregoing statements with respect to the behavior of indicators

present the subject in its simplest terms. Many substances other than

those named may be employed, and they have been carefully studied to

determine the exact concentration of H^{+} ions at which the color

change of each occurs. It is thus possible to select an indicator

for a particular purpose with considerable accuracy. As data of this

nature do not belong in an introductory manual, reference is made to

the following papers or books in which a more extended treatment of

the subject may be found:

Washburn, E.W., Principles of Physical Chemistry (McGraw-Hill Book

Co.), (Second Edition, 1921), pp. 380-387.

Prideaux, E.B.R., The Theory and Use of Indicators (Constable & Co.,

Ltd.), (1917).

Salm, E., A Study of Indicators, !Z. physik. Chem.!, 57 (1906),

471-501.

Stieglitz, J., Theories of Indicators, !J. Am. Chem. Soc.!, 25 (1903),

1112-1127.

Noyes, A.A., Quantitative Applications of the Theory of Indicators to

Volumetric Analysis, !J. Am. Chem. Soc.!, 32 (1911), 815-861.

Bjerrum, N., General Discussion, !Z. Anal. Chem.!, 66 (1917), 13-28

and 81-95.

Ostwald, W., Colloid Chemistry of Indicators, !Z. Chem. Ind.

Kolloide!, 10 (1912), 132-146.

[Note 1: Glaser, !Indikatoren der Acidimetrie und Alkalimetrie!.

Wiesbaden, 1901.]

PREPARATION OF INDICATOR SOLUTIONS

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.

A good grade of material 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 very 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.

A !phenolphthalein solution! is prepared by dissolving 1 gram of the

pure compound in 100 cc. of 95 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

boiling 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. Soluble litmus tablets are

often obtainable, but the litmus as commonly supplied to the market is

mixed with calcium carbonate or sulphate and compressed into lumps. To

prepare a solution, these are powdered and treated two or three times

with alcohol, 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 95 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 just produce a distinct color. This solution must be kept in an

unstoppered bottle. It should 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 phenolphthalein is to be preferred.

PREPARATION OF STANDARD SOLUTIONS

!Hydrochloric Acid and Sodium Hydroxide. Approximate Strength!, 0.5 N

PROCEDURE.--Measure out 40 cc. of concentrated, pure hydrochloric

acid into a clean liter bottle, and dilute with distilled water to an

approximate volume of 1000 cc. Shake the solution vigorously 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 (Note 1).

Weigh out, upon a rough balance, 23 grams of sodium hydroxide (Note

2). Dissolve the hydroxide in water in a beaker. Pour the solution

into a liter bottle and dilute, as above, to approximately 1000 cc.

This bottle should preferably have a rubber stopper, as the hydroxide

solution attacks the glass of the ground joint of a glass stopper, and

may cement the stopper to the bottle. Shake the solution as described

above.

[Note 1: The original solutions are prepared of a strength greater

than 0.5 N, as they are more readily diluted than strengthened if

later adjustment is desired.

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.]

[Note 2: Commercial sodium hydroxide is usually impure and always

contains more or less carbonate; an allowance is therefore made for

this impurity by placing the weight taken at 23 grams per liter. If

the hydroxide is known to be pure, a lesser amount (say 21 grams) will

suffice.]

COMPARISON OF ACID AND ALKALI SOLUTIONS

PROCEDURE.--Rinse a previously calibrated burette three times with the

hydrochloric acid solution, using 10 cc. each time, and allowing the

liquid to run out through the tip to displace all water and air

from that part of the burette. Then fill the burette with the acid

solution. Carry out the same procedure with a second burette, using

the sodium hydroxide solution.

The acid solution may be placed in a plain or in a glass-stoppered

burette as may be more convenient, but the alkaline solution should

never be allowed to remain long in a glass-stoppered burette, as it

tends to cement the stopper to the burette, rendering it useless. It

is preferable to use a plain burette for this solution.

When the burettes are ready for use and all air bubbles displaced from

the tip (see Note 2, page 17) note the exact position of the liquid in

each, and record the readings in the notebook. (Consult page 188.) Run

out from the burette into a beaker about 40 cc. of the acid 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, stirring

constantly, 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 drop of either solutions served

to produce a distinct change of color. Select as the final 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 (Note 1). If the titration has occupied more

than the three minutes required for draining the sides of the burette,

the final reading may be taken immediately and recorded in the

notebook.

Refill the burettes and repeat the titration. From the records of

calibration already obtained, correct the burette readings and make

corrections for temperature, if necessary. 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

of the two titrations should not vary by more than two parts in one

thousand (Note 2). If the variation in results is greater than this,

refill the burettes and repeat the titration until satisfactory values

are obtained. Use a new page in the notebook for each titration.

Inaccurate values should not be erased or discarded. They should be

retained and marked "correct" or "incorrect," as indicated by the

final outcome of the titrations. This custom should be rigidly

followed in all analytical work.

[Note 1: 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.]

[Note 2: While variation of two parts in one thousand in the values

obtained by an inexperienced analyst is not excessive, 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, but these are rare and can only

be recognized by an experienced analyst. It is essential that the

beginner should acquire at least the degree of accuracy indicated if

he is to become a successful analyst.]

STANDARDIZATION OF HYDROCHLORIC ACID

SELECTION AND PREPARATION OF STANDARD

The selection of the best substance to be used as a standard for acid

solutions has been the subject of much controversy. The work of Lunge

(!Ztschr. angew. Chem.! (1904), 8, 231), Ferguson (!J. Soc. Chem.

Ind.! (1905), 24, 784), and others, seems to indicate that the best

standard is sodium carbonate prepared from sodium bicarbonate by

heating the latter at temperature 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\_{2}CO\_{3} + H\_{2}O + CO\_{2}

and without loss of any carbon dioxide from the sodium carbonate, such

as may occur at higher temperatures. The process is carried out as

described below.

PROCEDURE.--Place in a porcelain crucible about 6 grams (roughly

weighed) of the purest sodium bicarbonate obtainable. Rest the

crucible upon a triangle of iron or copper wire so placed within a

large crucible that there is an open air space of about three eighths

of an inch between them. The larger crucible may be of iron, nickel or

porcelain, as may be most convenient. Insert the bulb of a thermometer

reading to 350°C. in the bicarbonate, supporting it with 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 porcelain crucible, which now contains sodium carbonate,

to a desiccator. When it is cold, transfer the carbonate to a

stoppered weighing tube or weighing-bottle.

STANDARDIZATION

PROCEDURE.--Clean carefully the outside of a weighing-tube, or

weighing-bottle, containing the pure sodium carbonate, taking care

to handle it as little as possible after wiping. Weigh the tube

accurately to 0.0001 gram, and record the weight in the notebook. Hold

the tube over the top of a beaker (200-300 cc.) and cautiously remove

the stopper, making sure that no particles fall from it or from the

tube elsewhere than in the beaker. Pour out from the tube a portion

of the carbonate, replace the stopper and determine approximately how

much has been removed. Continue this procedure until 1.00 to 1.10

grams has been taken from the tube. Then weigh the tube accurately

and record the weight under the first weight in the notebook.

The difference in the two weights is the weight of the carbonate

transferred to the beaker. Proceed in the same way to transfer a

second portion of the carbonate from the tube to another beaker of

about the same size as the first. The beakers should be labeled and

plainly marked to correspond with the entries in the notebook.

Pour over the carbonate in each beaker 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 on page 37. Note the

readings of the burettes after the proper interval, and record them in

the notebook. Repeat the procedure, using the second portion of sodium

carbonate. Apply the necessary calibration corrections to the volumes

of the solutions used, and correct for temperature if necessary.

From the data obtained, calculate the volume of the hydrochloric

acid solution which is equivalent to the volume of sodium hydroxide

solution used in this titration. Subtract this volume from the volume

of hydrochloric acid. The difference represents the volume of acid

used to react with the sodium carbonate. Divide the weight of sodium

carbonate by this volume in cubic centimeters, thus obtaining the

weight of sodium carbonate equivalent to each cubic centimeter of the

acid.

From this weight it is possible to calculate the corresponding weight

of HCl in each cubic centimeter of the acid, and in turn the relation

of the acid to the normal.

If, however, it is recalled that normal solutions are equivalent to

each other, it will be seen that the same result may be more readily

reached by dividing the weight in grams of sodium carbonate per cubic

centimeter just found by titration by the weight which would be

contained in the same volume of a normal solution of sodium carbonate.

A normal solution of sodium carbonate contains 53.0 grams per liter,

or 0.0530 gram per cc. (see page 29). The relation of the acid

solution to the normal is, therefore, calculated by dividing the

weight of the carbonate to which each cubic centimeter of the acid is

equivalent by 0.0530. The standardization must be repeated until the

values obtained agree within, at most, two parts in one thousand.

When the standard of the acid solution has been determined, calculate,

from the known ratio of the two solutions, the relation of the sodium

hydroxide solution to a normal solution (Notes 1 and 2).

[Note 1: In the foregoing procedure the acid solution is standardized

and the alkali solution referred to this standard by calculation. It

is equally possible, if preferred, to standardize the alkali solution.

The standards in a common use for this purpose are purified

oxalic acid (H\_{2}C\_{2}O\_{4}.2H\_{2}O), potassium acid oxalate

(KHC\_{2}O\_{4}.H\_{2}O or KHC\_{2}O\_{4}), potassium tetroxalate

(KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O), or potassium acid tartrate

(KHC\_{4}O\_{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, therefore, as monobasic acids, and the

tetroxalate as a tribasic acid.]

[Note 2: 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 to be described later. 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.]

DETERMINATION OF THE TOTAL ALKALINE STRENGTH OF SODA ASH

Soda ash is crude sodium carbonate. If made by the ammonia process it

may contain also sodium chloride, sulphate, and hydroxide; when made

by the Le Blanc process it may contain sodium sulphide, silicate, and

aluminate, and other impurities. Some of these, notably the hydroxide,

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.

PROCEDURE.--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. This is accomplished as follows: Weigh out on an analytical

balance two samples of soda ash of about 5 grams each into beakers

of about 500 cc. capacity. (The weighings need be made to centigrams

only.) Dissolve the ash in 75 cc. of water, warming gently, and filter

off the insoluble residue; wash the filter by filling it at least

three times with distilled water, and allowing it to drain, adding the

washings to the main filtrate. Cool the filtrate to approximately the

standard temperature of the laboratory, and transfer it to a 250 cc.

measuring flask, washing out the beaker thoroughly. Add distilled

water of laboratory temperature 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 the solution in a measuring flask, or

pipette, either of which before use should, unless they are dry on the

inside, be rinsed out with at least two small portions of the soda ash

solution to displace any water.

If a flask is used, fill it to the graduation with the soda ash

solution and remove any liquid from the neck above the graduation with

filter paper. Empty it into a beaker, and wash out the small flask,

unless it is graduated for !delivery!, using small quantities of

water, which are added to the liquid in the beaker. A second 50 cc.

portion from the main solution should be measured off into a second

beaker. Dilute the solutions in each beaker to 100 cc., add two drops

of a solution of methyl orange (Note 1) and titrate for the alkali

with the standard hydrochloric acid solution, using the alkali

solution to complete the titration as already prescribed.

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 (Note 2).

[Note 1: The hydrochloric acid sets free carbonic acid which is

unstable and breaks down into water and carbon dioxide, most of which

escapes from the solution. Carbonic acid is a weak acid and, as such,

does not yield a sufficient concentration of H^{+} ions to cause the

indicator to change to a pink (see page 32).

The chemical changes involved may be summarized as follows:

2H^{+}, 2Cl^{-} + 2Na^{+}, CO\_{3}^{--} --> 2Na^{+}, 2Cl^{-} +

[H\_{2}CO\_{3}] --> H\_{2}O + CO\_{2}]

[Note 2: A determination of the alkali present as hydroxide in soda

ash may be determined by precipitating the carbonate by the addition

of barium chloride, removing the barium carbonate by filtration, and

titrating the alkali in the filtrate.

The caustic alkali may also be determined by first using

phenolphthalein as an indicator, which will show by its change from

pink to colorless the point at which the caustic alkali has been

neutralized and the carbonate has been converted to bicarbonate, and

then adding methyl orange and completing the titration. The amount of

acid necessary to change the methyl orange to pink is a measure of one

half of the carbonate present. The results of the double titration

furnish the data necessary for the determination of the caustic alkali

and of the carbonate in the sample.]

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. Add two drops of

phenolphthalein 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 (Note 1). 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 (Note 2). If no color reappears during this time,

complete the titration in the hot solution. 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.

From the corrected volume of alkali required to react with the

oxalic acid, calculate the percentage of the crystallized acid

(H\_{2}C\_{2}O\_{4}.2H\_{2}O) in the sample (Note 3).

[Note 1: All commercial caustic soda such as that from which the

standard solution was made contains some sodium carbonate. This reacts

with the oxalic acid, setting free carbonic acid, which, in turn,

forms sodium bicarbonate with the remaining carbonate:

H\_{2}CO\_{3} + Na\_{2}CO\_{3} --> 2HNaCO\_{3}.

This compound does not hydrolyze sufficiently to furnish enough OH^{-}

ions to cause phenolphthalein to remain pink; hence, the color of

the indicator is discharged in cold solutions at the point at which

bicarbonate is formed. If, however, the solution is heated to boiling,

the bicarbonate loses carbon dioxide and water, and reverts to sodium

carbonate, which causes the indicator to become again pink:

2HNaCO\_{3} --> H\_{2}O + CO\_{2} + Na\_{2}CO\_{3}.

By adding successive portions of hydrochloric acid and boiling, the

carbonate is ultimately all brought into reaction.

The student should make sure that the difference in behavior of the

two indicators, methyl orange and phenolphthalein, is understood.]

[Note 2: 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 should not be greater than 0.3-0.4 cc.]

[Note 3: Attention has already been called to the fact that the color

changes in the different indicators occur at varying concentrations

of H^{+} or OH^{-} ions. They do not indicate exact theoretical

neutrality, but a particular indicator always shows its color change

at a particular concentration of H^{+} or OH^{-} ions. The results

of titration with a given indicator are, therefore, comparable. As a

matter of fact, a small error is involved in the procedure as outlined

above. The comparison of the acid and alkali solutions was made, using

methyl orange as an indicator, while the titration of the oxalic acid

is made with the use of phenolphthalein. For our present purposes the

small error may be neglected but, if time permits, the student is

recommended to standardize the alkali solution against one of the

substances named in Note 1, page 41, and also to ascertain

the comparative value of the acid and alkali solutions, using

phenolphthalein as indicator throughout, and conducting the titrations

as described above. This will insure complete accuracy.]

II. OXIDATION PROCESSES

GENERAL DISCUSSION

In the oxidation processes of volumetric analysis standard solutions

of oxidizing agents and of reducing agents take the place of the acid

and alkali solutions of the neutralization processes already studied.

Just as an acid solution was the principal reagent in alkalimetry, and

the alkali solution used only to make certain of the end-point, the

solution of the oxidizing agent is the principal reagent for the

titration of substances exerting a reducing action. It is, in general,

true that oxidizable substances are determined by !direct! titration,

while oxidizing substances are determined by !indirect! titration.

The important oxidizing agents employed in volumetric solutions are

potassium bichromate, potassium permangenate, 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), may 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, or its derivatives;

iodine and sodium thiosulphate; hypochlorites and arsenious acid.

BICHROMATE PROCESS FOR THE DETERMINATION OF IRON

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\_{2}Cr\_{2}O\_{7} + 14HCl --> 6FeCl\_{3} + 2CrCl\_{3} + 2KCl

+ 7H\_{2}O.

NORMAL SOLUTIONS OF OXIDIZING OR REDUCING AGENTS

It will be recalled that the system of normal solutions is based upon

the equivalence of the reagents which they contain to 8 grams of

oxygen or 1 gram of hydrogen. A normal solution of an oxidizing agent

should, therefore, contain that amount per liter which is equivalent

in oxidizing power to 8 grams of oxygen; a normal reducing solution

must be equivalent in reducing power to 1 gram of hydrogen. In order

to determine what the amount per liter will be it is necessary to know

how the reagents enter into reaction. The two solutions to be employed

in the process under consideration are those of potassium bichromate

and ferrous sulphate. The reaction between them, in the presence of an

excess of sulphuric acid, may be expressed as follows:

6FeSO\_{4} + K\_{2}Cr\_{2}O\_{7} + 7H\_{2}SO\_{4} --> 3Fe\_{2}(SO\_{4})\_{3} +

K\_{2}SO\_{4} + Cr\_{2}(SO\_{4})\_{3} + 7H\_{2}O.

If the compounds of iron and chromium, with which alone we are now

concerned, be written in such a way as to show the oxides of these

elements in each, they would appear as follows: On the left-hand side

of the equation 6(FeO.SO\_{3}) and K\_{2}O.2CrO\_{3}; on the right-hand

side, 3(Fe\_{2}O\_{3}.3SO\_{3}) and Cr\_{2}O\_{3}.3SO\_{3}. A careful

inspection shows that there are three less oxygen atoms associated

with chromium atoms on the right-hand side of the equation than on the

left-hand, but there are three more oxygen atoms associated with iron

atoms on the right than on the left. In other words, a molecule of

potassium bichromate has given up three atoms of oxygen for oxidation

purposes; i.e., a molecular weight in grams of the bichromate (294.2)

will furnish 3 X 16 or 48 grams of oxygen for oxidation purposes.

As this 48 grams is six times 8 grams, the basis of the system, the

normal solution of potassium bichromate should contain per liter one

sixth of 294.2 grams or 49.03 grams.

A further inspection of the dissected compounds above shows that six

molecules of FeO.SO\_{3} were required to react with the three atoms of

oxygen from the bichromate. From the two equations

3H\_{2} + 3O --> 3H\_{2}O

6(FeO.SO\_{3}) + 3O --> 3(Fe\_{2}O\_{3}.3SO\_{3})

it is plain that one molecule of ferrous sulphate is equivalent to one

atom of hydrogen in reducing power; therefore one molecular weight in

grams of ferrous sulphate (151.9) is equivalent to 1 gram of

hydrogen. Since the ferrous sulphate crystalline form has the formula

FeSO\_{4}.7H\_{2}O, a normal reducing solution of this crystalline salt

should contain 277.9 grams per liter.

PREPARATION OF SOLUTIONS

!Approximate Strength 0.1 N!

It is possible to purify commercial potassium bichromate by

recrystallization from hot water. It must then be dried and cautiously

heated to fusion to expel the last traces of moisture, but not

sufficiently high to expel any oxygen. The pure salt thus prepared,

may be weighed out directly, dissolved, and the solution diluted in a

graduated flask to a definite volume. In this case no standardization

is made, as the normal value can be calculated directly. It is,

however, more generally customary to standardize a solution of

the commercial salt by comparison with some substance of definite

composition, as described below.

PROCEDURE.--Pulverize about 5 grams of potassium bichromate of good

quality. Dissolve the bichromate in distilled water, transfer the

solution to a liter bottle, and dilute to approximately 1000 cc. Shake

thoroughly until the solution is uniform.

To prepare the solution of the reducing agent, pulverize about 28

grams of ferrous sulphate (FeSO\_{4}.7H\_{2}O) or about 40 grams of

ferrous ammonium sulphate (FeSO\_{4}.(NH\_{4})\_{2}SO\_{4}.6H\_{2}O) and

dissolve in distilled water containing 5 cc. of concentrated sulphuric

acid. Transfer the solution to a liter bottle, add 5 cc. concentrated

sulphuric acid, make up to about 1000 cc. and shake vigorously to

insure uniformity.

INDICATOR SOLUTION

No indicator is known which, like methyl orange, can be used within

the solution, to show when the oxidation process is complete. Instead,

an outside indicator solution is employed to which drops of the

titrated solution are transferred for testing. The reagent used is

potassium ferricyanide, which produces a blue precipitate (or color)

with ferrous compounds as long as there are unoxidized ferrous ions in

the titrated solution. Drops of the indicator solution are placed upon

a glazed porcelain tile, or upon white cardboard which has been coated

with paraffin to render it waterproof, and drops of the titrated

solution are transferred to the indicator on the end of a stirring

rod. When the oxidation is nearly completed only very small amounts

of the ferrous compounds remain unoxidized and the reaction with the

indicator is no longer instantaneous. It is necessary to allow a brief

time to elapse before determining that no blue color is formed. Thirty

seconds is a sufficient interval, and should be adopted throughout the

analytical procedure. If left too long, the combined effect of light

and dust from the air will cause a reduction of the ferric compounds

already formed and a resultant blue will appear which misleads the

observer with respect to the true end-point.

The indicator solution must be highly diluted, otherwise its own color

interferes with accurate observation. Prepare a fresh solution, as

needed each day, by dissolving a crystal of potassium ferricyanide

about the size of a pin's head in 25 cc. of distilled water. The salt

should be carefully tested with ferric chloride for the presence of

ferrocyanides, which give a blue color with ferric salts.

In case of need, the ferricyanide can be purified by adding to its

solution a little bromine water and recrystallizing the compound.

COMPARISON OF OXIDIZING AND REDUCING SOLUTIONS

PROCEDURE.--Fill one burette with each of the solutions, observing

the general procedure with respect to cleaning and rinsing already

prescribed. The bichromate solution is preferably to be placed in a

glass-stoppered burette.

Run out from a burette into a beaker of about 300 cc. capacity nearly

40 cc. of the ferrous solution, add 15 cc. of dilute hydrochloric acid

(sp. gr. 1.12) and 150 cc. of water and run in the bichromate

solution from another burette. Since both solutions are approximately

tenth-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, mixing it with a drop of

indicator on the tile (Note 1). If a blue precipitate appears at once,

0.5 cc. of the bichromate solution may be added 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. 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, a little more of the

ferrous solution may be added and the end-point definitely fixed.

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.

[Note 1: 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 ferrous 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. This cautious

removal of solution does not seriously affect the accuracy of the

determination, as it will be noted that the volume of the titrated

solution is about 200 cc. and the portions removed are very

small. Moreover, if the procedure is followed as prescribed, the

concentration of unoxidized iron decreases very rapidly as the

titration is carried out so that when the final tests are made, though

large drops may be taken, the amount of ferrous iron is not sufficient

to produce any appreciable error in results.

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.]

STANDARDIZATION OF POTASSIUM BICHROMATE SOLUTIONS

!Selection of a Standard!

A substance which will serve satisfactorily as a standard for

oxidizing solutions must possess certain specific properties: It must

be of accurately known composition and definite in its behavior as a

reducing agent, and it must be permanent against oxidation in the air,

at least for considerable periods. Such standards may take the form of

pure crystalline salts, such as ferrous ammonium sulphate, or may be

in the form of iron wire or an iron ore of known iron content. It is

not necessary that the standard should be of 100 per cent purity,

provided the content of the active reducing agent is known and no

interfering substances are present.

The two substances most commonly used as standards for a bichromate

solution are ferrous ammonium sulphate and iron wire. A standard wire

is to be purchased in the market which answers the purpose well, and

its iron content may be determined for each lot purchased by a number

of gravimetric determinations. It may best be preserved in jars

containing calcium chloride, but this must not be allowed to come

into contact with the wire. It should, however, even then be examined

carefully for rust before use.

If pure ferrous ammonium sulphate is used as the standard, clear

crystals only should be selected. It is perhaps even better to

determine by gravimetric methods once for all the iron content of a

large commercial sample which has been ground and well mixed. This

salt is permanent over long periods if kept in stoppered containers.

STANDARDIZATION

PROCEDURE.--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 filter paper (not touched by the fingers), should

be weighed on a watch-glass, and be bent in such a way as not to

interfere with the movement of the balance.

Place 30 cc. of hydrochloric acid (sp. gr. 1.12) in each of two 300

cc. Erlenmeyer flasks, 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

solution. Boil for two or three minutes, keeping the flasks covered

(Note 1), then wash the sides of the flasks 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 (Note 2). 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 (Note 3), add about 35 cc. of

the standard solution at once and finish the titration as prescribed

above, making use of the ferrous solution if the end-point should be

passed.

From the corrected volumes of the bichromate solution required to

oxidize the iron actually know to be present in the wire, calculate

the relation of the standard solution to the normal.

Repeat the standardization until the results are concordant within at

least two parts in one thousand.

[Note 1: The hydrochloric acid is added to the ferrous solution

to insure the presence of at least sufficient free acid for the

titration, as required by the equation on page 48.

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.]

[Note 2: It is plain that all the iron must be reduced to the ferrous

condition before the titration begins, as some oxidation may have

occurred from the oxygen of the air during solution. It is also

evident that any excess of the agent used to reduce the iron must be

removed; otherwise it will react with the bichromate added later.

The reagents available for the reduction of 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

mercuric salts have no effect upon ferrous iron or the bichromate. The

reactions involved are:

2FeCl\_{3} + SnCl\_{2} --> 2FeCl\_{2} + SnCl\_{4}

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.]

[Note 3: 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.]

DETERMINATION OF IRON IN LIMONITE

PROCEDURE.--Grind the mineral (Note 1) to a fine powder. Weigh out

accurately two portions of about 0.5 gram (Note 2) into 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 dilute 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 the residue is white,

or known to be free from iron, it may be neglected and need not be

removed by filtration. If a dark residue remains, collect it on a

filter, wash free from hydrochloric acid, and ignite the filter in a

platinum crucible (Note 3). Mix the ash with five times its weight of

sodium carbonate and heat to fusion; cool, and disintegrate the fused

mass with boiling water in the crucible. Unite this solution and

precipitate (if any) with the acid solution, taking care to avoid loss

by effervescence. Wash out the crucible, heat the acid solution

to boiling, add stannous chloride solution until it is colorless,

avoiding a large excess (Note 4); cool, and when !cold!, add 40 cc. of

mercuric chloride solution, dilute to 200 cc., and proceed with the

titration as already described.

From the standardization data already obtained, and the known weight

of the sample, calculate the percentage of iron (Fe) in the limonite.

[Note 1: Limonite is selected as a representative of iron ores in

general. It 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.]

[Note 2: 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.]

[Note 3: A platinum crucible may be used for the roasting of the

limonite and must be used for the fusion of the residue. When used, it

must not be allowed to remain in the acid solution of ferric chloride

for any length of time, since the platinum is attacked and dissolved,

and the platinic chloride is later reduced by the stannous chloride,

and in the reduced condition reacts with the bichromate, thus

introducing an error. It should also be noted that copper and antimony

interfere with the determination of iron by the bichromate process.]

[Note 4: 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 already in the

ferrous condition. It should, however, be added from a dropper to

avoid an unnecessary excess.]

DETERMINATION OF CHROMIUM IN CHROME IRON ORE

PROCEDURE.--Grind the chrome iron ore (Note 1) in an agate mortar

until no grit is perceptible under the pestle. Weigh out two portions

of 0.5 gram each into iron crucibles which have been scoured inside

until bright (Note 2). Weigh out on a watch-glass (Note 3), using the

rough 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 (Note 4). Maintain

the fusion for five minutes, and stir constantly with a stout iron

wire, but do not raise the temperature above moderate redness (Notes 5

and 6).

Allow the crucible to cool until it can be comfortably handled (Note

7) and then place it in a 300 cc. beaker, and cover it with distilled

water (Note 8). 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

!while still alkaline! to boiling for fifteen minutes. Allow the

liquid to cool for a few minutes; then acidify with dilute sulphuric

acid (1:5), adding 10 cc. in excess of the amount necessary to

dissolve the ferric hydroxide (Note 9). Dilute to 200 cc., cool, add

from a burette an excess of a standard ferrous solution, and titrate

for the excess with a standard solution of potassium bichromate, using

the outside indicator (Note 10).

From the corrected volumes of the two standard solutions, and their

relations to normal solutions, calculate the percentage of chromium in

the ore.

[Note 1: Chrome iron ore is essentially a ferrous chromite, or

combination of FeO and Cr\_{2}O\_{3}. It must be reduced to a state of

fine subdivision to ensure a prompt reaction with the flux.]

[Note 2: The scouring of the iron crucible is rendered much easier if

it is first heated to bright redness and plunged into cold water. In

this process oily matter is burned off and adhering scale is caused to

chip off when the hot crucible contracts rapidly in the cold water.]

[Note 3: Sodium peroxide must be kept off of balance pans and should

not be weighed out on paper, as is the usual practice in the rough

weighing of chemicals. If paper to which the peroxide is adhering is

exposed to moist air it is likely to take fire as a result of

the absorption of moisture, and consequent evolution of heat and

liberation of oxygen.]

[Note 4: The lamp should never be allowed to remain under the

crucible, as this will raise the temperature to a point at which the

crucible itself is rapidly attacked by the flux and burned through.]

[Note 5: The sodium peroxide acts as both a flux and an oxidizing

agent. The chromic oxide is dissolved by the flux and oxidized to

chromic anhydride (CrO\_{3}) which combines with the alkali to form

sodium chromate. The iron is oxidized to ferric oxide.]

[Note 6: 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 a nickel crucible.

The peroxide must be dry, and must be protected from any admixture of

dust, paper, or of organic matter of any kind, otherwise explosions

may ensue.]

[Note 7: 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, which by slowly dissolving in acid form ferrous sulphate,

which reduces the chromate.]

[Note 8: Upon treatment with water the chromate passes into solution,

the ferric hydroxide remains undissolved, and the excess of peroxide

is decomposed with the evolution of oxygen. The subsequent boiling

insures the complete decomposition of the peroxide. Unless this is

complete, hydrogen peroxide is formed when the solution is acidified,

and this reacts with the bichromate, reducing it and introducing a

serious error.]

[Note 9: The addition of the sulphuric acid converts the sodium

chromate to bichromate, which behaves exactly like potassium

bichromate in acid solution.]

[Note 10: 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\_{2}O\_{3} may be weighed out

and dissolved in sulphuric acid; after reduction of all the iron by

stannous chloride and the addition of mercuric chloride, 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

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\_{2}S\_{4} --> 5Fe\_{2}(SO\_{4})\_{3} +

K\_{2}SO\_{4} + 2MnSO\_{4} + 8H\_{2}O

5C\_{2}H\_{2}O\_{4}(2H\_{2}O) + 2KMnO\_{4} +3H\_{2}SO\_{4} --> K\_{2}SO\_{4} +

2MnSO\_{4} + 10CO\_{2} + 1 H\_{2}O.

These are the fundamental reactions upon which the extensive use of

potassium permanganate depends; but besides 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 quantitatively

with the permanganate, as is the case with oxalic acid and the

oxalates.

Potassium permanganate is acted upon by hydrochloric acid; the action

is rapid in hot or concentrated solution (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.

However, the greater solubility of iron compounds in hydrochloric acid

makes it desirable to use this acid as a solvent, and experiments made

with this end in view have shown that in cold, dilute hydrochloric

acid solution, to which considerable quantities of manganous sulphate

and an excess of phosphoric acid have been added, it is possible to

obtain satisfactory results.

It is also possible to replace the hydrochloric acid by evaporating

the solutions with an excess of sulphuric acid until the latter fumes.

This procedure is somewhat more time-consuming, but the end-point of

the permanganate titration is more permanent. Both procedures are

described below.

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 pink

color of the solution.

PREPARATION OF A STANDARD SOLUTION

!Approximate Strength 0.1 N!

A study of the reactions given above which represent the oxidation of

ferrous compounds by potassium permanganate, shows that there are 2

molecules of KMnO\_{4} and 10 molecules of FeSO\_{4} on the

left-hand side, and 2 molecules of MnSO\_{4} and 5 molecules of

Fe\_{2}(SO\_{4})\_{5} on the right-hand side. Considering only these

compounds, and writing the formulas in such a way as to show the

oxides of the elements in each, the equation becomes:

K\_{2}O.Mn\_{2}O\_{7} + 10(FeO.SO\_{3}) --> K\_{2}O.SO\_{3} + 2(MnO.SO\_{3})

+ 5(Fe\_{2}O\_{3}.3SO\_{3}).

From this it appears that two molecules of KMnO\_{4} (or 316.0 grams)

have given up five atoms (or 80 grams) of oxygen to oxidize the

ferrous compound. Since 8 grams of oxygen is the basis of normal

oxidizing solutions and 80 grams of oxygen are supplied by 316.0 grams

of KMnO\_{4}, the normal solution of the permanganate should contain,

per liter, 316.0/10 grams, or 31.60 grams (Note 1).

The preparation of an approximately tenth-normal solution of the

reagent may be carried out as follows:

PROCEDURE.--Dissolve about 3.25 grams of potassium permanganate

crystals in approximately 1000 cc. of distilled water in a large

beaker, or casserole. Heat slowly and when the crystals have

dissolved, boil the solution for 10-15 minutes. Cover the solution

with a watch-glass; allow it to stand until cool, or preferably over

night. Filter the solution through a layer of asbestos. Transfer the

filtrate to a liter bottle and mix thoroughly (Note 2).

[Note 1: The reactions given on page 61 are those which take place in

the presence of an excess of acid. In neutral solutions the reduction

of the permanganate is less complete, and, under these conditions,

two gram-molecular weights of KMnO\_{4} will furnish only 48 grams

of oxygen. A normal solution for use under these conditions should,

therefore, contain 316.0/6 grams, or 52.66 grams.]

[Note 2: Potassium permanganate solutions are not usually stable for

long periods, and change more rapidly when first prepared than after

standing some days. This change 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 be protected from light and heat as far as possible, since both

induce decomposition with a deposition of manganese dioxide, and it

has been shown that 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 boil and filter solutions through

asbestos before standardization, as prescribed above. Such solutions

are relatively stable.]

COMPARISON OF PERMANGANATE AND FERROUS SOLUTIONS

PROCEDURE.--Fill a glass-stoppered burette with the permanganate

solution, observing the usual precautions, and fill a second burette

with the ferrous sulphate solution prepared for use with the potassium

bichromate. The permanganate solution cannot be used 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. Run out into a beaker about 40 cc. of the ferrous solution,

dilute to about 100 cc., add 10 cc. of dilute sulphuric acid, and run

in the permanganate solution to a slight permanent pink. Repeat, until

the ratio of the two solutions is satisfactorily established.

STANDARDIZATION OF A POTASSIUM PERMANGANATE SOLUTION

!Selection of a Standard!

Commercial potassium permanganate is rarely sufficiently pure to admit

of its direct weighing as a standard. On this account, and because

of the uncertainties as to the permanence of its solutions, it is

advisable to standardize them against substances of known value. Those

in most common use are iron wire, ferrous ammonium sulphate, sodium

oxalate, oxalic acid, and some other derivatives of oxalic acid.

With the exception of sodium oxalate, these all contain water of

crystallization which may be lost on standing. They should, therefore,

be freshly prepared, and with great care. At present, sodium oxalate

is considered to be one of the most satisfactory standards.

!Method A!

!Iron Standards!

The standardization processes employed when iron or its compounds are

selected as standards differ from those applicable in connection with

oxalate standards. The procedure which immediately follows is that in

use with iron standards.

As in the case of the bichromate process, it is necessary to reduce

the iron completely to the ferrous condition before titration. The

reducing agents available are zinc, sulphurous acid, or sulphureted

hydrogen. Stannous chloride may also be used when the titration is

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 both the removal of the excess and

the reoxidation of the iron, zinc or stannous chlorides are the most

satisfactory agents. For prompt and complete reduction it is essential

that the iron solution should be brought into ultimate contact with

the zinc. This is brought about by the use of a modified Jones

reductor, as shown in Figure 1. This reductor is a standard apparatus

and is used in other quantitative processes.

[Illustration: Fig. 1]

The tube A has an inside diameter of 18 mm. and is 300 mm. long; the

small tube has an inside diameter of 6 mm. and extends 100 mm. below

the stopcock. At the base of the tube A are placed some pieces of

broken glass or porcelain, covered by a plug of glass wool about 8 mm.

thick, and upon this is placed a thin layer of asbestos, such as is

used for Gooch filters, 1 mm. thick. The tube is then filled with the

amalgamated zinc (Note 1) to within 50 mm. of the top, and on the zinc

is placed a plug of glass wool. If the top of the tube is not already

shaped like the mouth of a thistle-tube (B), a 60 mm. funnel 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. After

preparation for use, or when left standing, the tube A should be

filled with water, to prevent clogging of the zinc.

[Note 1: The use of fine zinc in the reductor is not necessary and

tends to clog the tube. Particles which will pass a 10-mesh sieve, but

are retained by one of 20 meshes to the inch, are most satisfactory.

The zinc can be amalgamated by stirring or shaking it in a mixture of

25 cc. of normal mercuric chloride solution, 25 cc. of hydrochloric

acid (sp. gr. 1.12) and 250 cc. of water for two minutes. The solution

should then be poured off and the zinc thoroughly washed. It is then

ready for bottling and preservation under water. A small quantity of

glass wool is placed in the neck of the funnel to hold back foreign

material when the reductor is in use.]

STANDARDIZATION

PROCEDURE.--Weigh out into Erlenmeyer flasks 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 has dissolved to remove any volatile

hydrocarbons. Meanwhile prepare the reductor for use as follows:

Connect the vacuum bottle with the suction pump and pour into the

funnel at the top warm, dilute sulphuric acid, prepared by adding 5

cc. of concentrated sulphuric acid to 100 cc. of distilled water. See

that the stopcock (C) is open far enough to allow the acid to run

through slowly. Continue to pour in acid until 200 cc. have passed

through, then close the stopcock !while a small quantity of liquid

is still left in the funnel!. Discard 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, until assured that the zinc is not

contaminated with appreciable quantities of reducing substances. Be

sure that no air enters the reductor (Note 1).

Pour the iron solution while hot (but not boiling) through the

reductor at a rate not exceeding 50 cc. per minute (Notes 2 and 3).

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 (Note 4), 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 vacuum flask. Should the end-point be overstepped, the

ferrous sulphate solution may be added.

From the volume of the solution required to oxidize the iron in

the wire, calculate the relation to the normal of the permanganate

solution. The duplicate results should be concordant within two parts

in one thousand.

[Note 1: The funnel of the reductor must never be allowed to empty.

If it is left partially filled with water 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. !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.]

[Note 2: The iron is reduced to the ferrous condition by contact with

the zinc. The active agent may be considered to be !nascent! hydrogen,

and it must be borne in mind that the visible bubbles are produced by

molecular hydrogen, which is without appreciable effect upon ferric

iron.

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 is also possible to reduce the iron by treatment with zinc in a

flask from which air is excluded. The zinc must be present in excess

of the quantity necessary to reduce the iron and is finally completely

dissolved. This method is, however, less convenient and more tedious

than the use of the reductor.]

[Note 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 the volume used should always be the same in the

standardizations and all subsequent analyses.]

[Note 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 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. It is wiser to

discard such results and repeat the process.]

[Note 5: The potassium permanganate may, of course, be diluted and

brought to an exactly 0.1 N solution from the data here obtained. The

percentage of iron in the iron wire must be taken into account in all

calculations.]

!Method B!

!Oxalate Standards!

PROCEDURE.--Weigh out two portions of pure sodium oxalate of 0.25-0.3

gram each into beakers of about 600 cc. capacity. Add about 400 cc. of

boiling water and 20 cc. of manganous sulphate solution (Note 1).

When the solution of the oxalate is complete, heat the liquid, if

necessary, until near its boiling point (70-90°C.) and run in the

standard permanganate solution drop by drop from a burette, stirring

constantly until an end-point is reached (Note 2). Make a blank test

with 20 cc. of manganous sulphate solution and a volume of distilled

water equal to that of the titrated solution to determine the volume

of the permanganate solution required to produce a very slight pink.

Deduct this volume from the amount of permanganate solution used in

the titration.

From the data obtained, calculate the relation of the permanganate

solution to the normal. The reaction involved is:

5Na\_{2}C\_{2}O\_{4} + 2KMnO\_{4} + 8H\_{2}SO\_{4} --> 5Na\_{2}SO\_{4} +

K\_{2}SO\_{4} + 2MnSO\_{4} + 10CO\_{2} + 8H\_{2}O

[Note 1: The manganous sulphate titrating solution is made by

dissolving 20 grams of MnSO\_{4} in 200 cubic centimeters of water and

adding 40 cc. of concentrated sulphuric acid (sp. gr. 1.84) and 40 cc.

or phosphoric acid (85%).]

[Note 2: The reaction between oxalates and permanganates takes place

quantitatively only in hot acid solutions. The temperatures must not

fall below 70°C.]

DETERMINATION OF IRON IN LIMONITE

!Method A!

The procedures, as here prescribed, are applicable to iron ores in

general, provided these ores contain no constituents which are reduced

by zinc or stannous chloride and reoxidized by permanganates. Many

iron ores contain titanium, and this element among others does

interfere with the determination of iron by the process described.

If, however, the solutions of such ores are treated with sulphureted

hydrogen or sulphurous acid, instead of zinc or stannous chloride to

reduce the iron, and the excess reducing agent removed by boiling, an

accurate determination of the iron can be made.

PROCEDURE.--Grind the mineral to a fine powder. Weigh out two portions

of about 0.5 gram each into small porcelain crucibles. Roast the ore

at dull redness for ten minutes (Note 1), allow the crucibles to cool,

and place them and their contents in casseroles containing 30 cc. of

dilute hydrochloric acid (sp. gr. 1.12).

Proceed with the solution of the ore, and the treatment of the

residue, if necessary, exactly as described for the bichromate process

on page 56. When solution is complete, add 6 cc. of concentrated

sulphuric acid to each casserole, and evaporate on the steam bath

until the solution is nearly colorless (Note 2). Cover the casseroles

and heat over the flame of the burner, holding the casserole in

the hand and rotating it slowly to hasten evaporation and prevent

spattering, until the heavy white fumes of sulphuric anhydride are

freely evolved (Note 3). 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 which has been previously

washed; 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 reductor flask, using the ferrous sulphate solution if

the end-point should be overstepped.

From the corrected volume of permanganate solution used, calculate the

percentage of iron (Fe) in the limonite.

[Note 1: The preliminary roasting is usually necessary because, even

though the sulphuric acid would subsequently char the carbonaceous

matter, certain nitrogenous bodies are not thereby rendered insoluble

in the acid, and would be oxidized by the permanganate.]

[Note 2: The temperature of the steam bath is not sufficient to

volatilize sulphuric acid. Solutions may, therefore, be left to

evaporate overnight without danger of evaporation to dryness.]

[Note 3: The hydrochloric acid, both free and combined, is displaced

by the less volatile sulphuric acid at its boiling point. Ferric

sulphate separates at this point, since there is no water to hold

it in solution and care is required to prevent bumping. The ferric

sulphate usually has a silky appearance and is easily distinguished

from the flocculent silica which often remains undissolved.]

!Zimmermann-Reinhardt Procedure!

!Method (B)!

PROCEDURE.--Grind the mineral to a fine powder. Weigh out two portions

of about 0.5 gram each into small porcelain crucibles. Proceed with

the solution of the ore, treat the residue, if necessary, and reduce

the iron by the addition of stannous chloride, followed by mercuric

chloride, as described for the bichromate process on page 56. Dilute

the solution to about 400 cc. with cold water, add 10 cc. of the

manganous sulphate titrating solution (Note 1, page 68) and titrate

with the standard potassium permanganate solution to a faint pink

(Note 1).

From the standardization data already obtained calculate the

percentage of iron (Fe) in the limonite.

[Note 1: It has already been noted that hydrochloric acid reacts

slowly in cold solutions with potassium permanganate. It is, however,

possible to obtain a satisfactory, although somewhat fugitive

end-point in the presence of manganous sulphate and phosphoric acid.

The explanation of the part played by these reagents is somewhat

obscure as yet. It is possible that an intermediate manganic compound

is formed which reacts rapidly with the ferrous compounds--thus in

effect catalyzing the oxidizing process.

While an excess of hydrochloric acid is necessary for the successful

reduction of the iron by stannous chloride, too large an amount

should be avoided in order to lessen the chance of reduction of the

permanganate by the acid during titration.]

DETERMINATION OF THE OXIDIZING POWER OF PYROLUSITE

INDIRECT OXIDATION

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 is reduced and

dissolved by an excess of ferrous sulphate or oxalic acid in the

presence of sulphuric acid, and the unused excess determined by

titration with standard permanganate solution.

PROCEDURE.--Grind the mineral in an agate mortar until no grit

whatever can be detected under the pestle (Note 1). Transfer it to a

stoppered weighing-tube, and weigh out two portions of about 0.5 gram

into beakers (400-500 cc.) Read Note 2, and then calculate in each

case the weight of oxalic acid (H\_{2}C\_{2}O\_{4}.2H\_{2}O) required to

react with the weights of pyrolusite taken. The reaction involved is

MnO\_{2} + H\_{2}C\_{2}O\_{4}(2H\_{2}O) + H\_{2}SO\_{4} --> MnSO\_{4} +

2CO\_{2} + 4H\_{2}O.

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. Pour into each beaker 25 cc. of

water and 50 cc. of dilute sulphuric acid (1:5), cover and warm the

beaker and its contents gently until the evolution of carbon dioxide

ceases (Note 3). If a residue remains which is sufficiently colored to

obscure the end-reaction of the permanganate, it must be removed by

filtration.

Finally, dilute the solution to 200-300 cc., heat the solution to a

temperature just below boiling, add 15 cc. of a manganese sulphate

solution and while hot, titrate for the excess of the oxalic acid with

standard permanganate solution (Notes 4 and 5).

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.

[Note 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.]

[Note 2: 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,

thus increasing the accuracy of the process. On the other hand, the

excess of oxalic acid should not be so large as to react with more of

the permanganate solution than is contained in a 50 cc. burette. If

the pyrolusite under examination is known to be of high grade, say 80

per cent pure, or above the calculation of the oxalic acid needed may

be based upon an assumption that the mineral is all MnO\_{2}. If the

quality of the mineral is unknown, it is better to weigh out three

portions instead of two and to add to one of these the amount of

oxalic prescribed, assuming complete purity of the mineral. Then run

in the permanganate solution from a pipette or burette to determine

roughly the amount required. If the volume exceeds the contents of a

burette, the amount of oxalic acid added to the other two portions is

reduced accordingly.]

[Note 3: 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.]

[Note 4: Ferrous ammonium sulphate, ferrous sulphate, or iron wire

may be substituted for the oxalic acid. The reaction is then the

following:

2 FeSO\_{4} + MnO\_{2} + 2H\_{2}SO\_{4} --> Fe\_{2}(SO\_{4})\_{3} + 2H\_{2}O

The excess of ferrous iron may also be determined by titration with

potassium bichromate, if desired. Care is required to prevent the

oxidation of the iron by the air, if ferrous salts are employed.]

[Note 5: The oxidizing power of pyrolusite may be determined by other

volumetric processes, one of which is outlined in the following

reactions:

MnO\_{2} + 4HCl --> MnCl\_{2} + Cl\_{2} + 2H\_{2}O

Cl\_{2} + 2KI --> I\_{2} + 2KCl

I\_{2} + 2Na\_{2}S\_{2}O\_{3} --> Na\_{2}S\_{4}O\_{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 78. This is a direct

process, although it involves three steps.]

IODIMETRY

The titration of iodine against sodium thiosulphate, with starch as an

indicator, may perhaps be regarded as the most accurate of volumetric

processes. The thiosulphate solution may be used in both acid and

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, as, for

example, in the process outlined in Note 5 on page 74.

The fundamental reaction upon which iodometric processes are based is

the following:

I\_{2} + 2 Na\_{2}S\_{2}O\_{3} --> 2 NaI + Na\_{2}S\_{4}O\_{6}.

This reaction between iodine and sodium thiosulphate, resulting in

the formation of the compound Na\_{2}S\_{4}O\_{6}, called sodium

tetrathionate, is quantitatively exact, and differs in that

respect from the action of chlorine or bromine, which oxidize the

thiosulphate, but not quantitatively.

NORMAL SOLUTIONS OF IODINE AND SODIUM THIOSULPHATE

If the formulas of sodium thiosulphate and sodium tetrathionate are

written in a manner to show the atoms of oxygen associated

with sulphur atoms in each, thus, 2(Na\_{2}).S\_{2}O\_{2} and

Na\_{2}O.S\_{4}O\_{5}, it is plain that in the tetrathionate there are

five atoms of oxygen associated with sulphur, instead of the four

in the two molecules of the thiosulphate taken together. Although,

therefore, the iodine contains no oxygen, the two atoms of iodine

have, in effect, brought about the addition of one oxygen atoms to the

sulphur atoms. That is the same thing as saying that 253.84 grams of

iodine (I\_{2}) are equivalent to 16 grams of oxygen; hence, since 8

grams of oxygen is the basis of normal solutions, 253.84/2 or 126.97

grams of iodine should be contained in one liter of normal iodine

solution. By a similar course of reasoning the conclusion is reached

that the normal solution of sodium thiosulphate should contain,

per liter, its molecular weight in grams. As the thiosulphate in

crystalline form has the formula Na\_{2}S\_{2}O\_{3}.5H\_{2}O, this weight

is 248.12 grams. Tenth-normal or hundredth-normal solutions are

generally used.

PREPARATION OF STANDARD SOLUTIONS

!Approximate Strength, 0.1 N!

PROCEDURE.--Weigh out on the rough 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. and transfer to a liter bottle and mix

thoroughly (Note 1).[1]

[Footnote 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 which

has been previously boiled and cooled, and dilute to 1000 cc., also

with boiled water. Transfer the solution to a liter bottle and mix

thoroughly (Note 2).

[Note 1: Iodine solutions react with water to form hydriodic acid

under the influence of the sunlight, and even at low room temperatures

the iodine tends to volatilize from solution. They should, therefore,

be protected from light and heat. Iodine solutions are not stable for

long periods under the best of conditions. They cannot be used in

burettes with rubber tips, since they attack the rubber.]

[Note 2: Sodium thiosulphate (Na\_{2}S\_{2}O\_{3}.5H\_{2}O) is

rarely wholly pure as sold commercially, but may be purified by

recrystallization. The carbon dioxide absorbed from the air by

distilled water decomposes the salt, with the separation of sulphur.

Boiled water which has been cooled out of contact with the air should

be used in preparing solutions.]

INDICATOR SOLUTION

The starch solution for use as an indicator must be freshly prepared.

A soluble starch is obtainable which serves well, and a solution of

0.5 gram of this starch in 25 cc. of boiling water is sufficient. The

solution should be filtered while hot and is ready for use when cold.

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 by filtration,

become so colored by the iodine that they are not readily decolorized

by the thiosulphate (Note 1).

[Note 1: The blue color which results when free iodine and starch

are brought together is probably not due to the formation of a true

chemical compound. It is regarded as a "solid solution" of iodine in

starch. Although it is unstable, and easily destroyed by heat, it

serves as an indicator for the presence of free iodine of remarkable

sensitiveness, and makes the iodometric processes the most

satisfactory of any in the field of volumetric analysis.]

COMPARISON OF IODINE AND THIOSULPHATE SOLUTIONS

PROCEDURE.--Place the solutions in burettes (the iodine in a

glass-stoppered burette), observing the usual precautions. 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.

STANDARDIZATION OF SOLUTIONS

Commercial iodine is usually not sufficiently pure to permit of its

use as a standard for thiosulphate solutions or the direct preparation

of a standard solution of iodine. It is likely to contain, beside

moisture, some iodine chloride, if chlorine was used to liberate the

iodine when it was prepared. It may be purified by sublimation after

mixing it with a little potassium iodide, which reacts with the iodine

chloride, forming potassium chloride and setting free the iodine. The

sublimed iodine is then dried by placing it in a closed container over

concentrated sulphuric acid. It may then be weighed in a stoppered

weighing-tube and dissolved in a solution of potassium iodide in a

stoppered flask to prevent loss of iodine by volatilization. About 18

grams of the iodide and twelve grams of iodine per liter are required

for an approximately tenth-normal solution.

An iodine solution made from commercial iodine may also be

standardized against arsenious oxide (As\_{4}O\_{6}). This substance

also usually requires purification by sublimation before use.

The substances usually employed for the standardization of a

thiosulphate solution are potassium bromate and metallic copper. The

former is obtainable in pure condition or may be easily purified by

re-crystallization. Copper wire of high grade is sufficiently pure

to serve as a standard. Both potassium bromate and cupric salts in

solution will liberate iodine from an iodide, which is then titrated

with the thiosulphate solution.

The reactions involved are the following:

(a) KBrO\_{3} + 6KI + 3H\_{2}SO\_{4} --> KBr + 3I\_{2} + 3K\_{2}SO\_{4} + 3H\_{2}O,

(b) 3Cu + 8HNO\_{3} --> 3Cu(NO\_{3})\_{2} + 2NO + 4H\_{2}O,

2Cu(NO\_{3})\_{2} + 4KI --> 2CuI + 4KNO\_{3} + I\_{2}.

Two methods for the direct standardization of the sodium thiosulphate

solution are here described, and one for the direct standardization of

the iodine solution.

!Method A!

PROCEDURE.--Weigh out into 500 cc. beakers two portions of about

0.150-0.175 gram of potassium bromate. Dissolve each of these in 50

cc. of water, and add 10 cc. of a potassium iodide solution containing

3 grams of the salt in that volume (Note 1). Add to the mixture 10 cc.

of dilute sulphuric acid (1 volume of sulphuric acid with 5 volumes of

water), allow the solution to stand for three minutes, and dilute to

150 cc. (Note 2). Run in thiosulphate solution from a burette until

the color of the liberated iodine is nearly destroyed, and 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

which is generally present in the potassium iodide solution, and

deduct this from the total volume used in the titration.

From the data obtained, calculate the relation of the thiosulphate

solution to a normal solution, and subsequently calculate the similar

value for the iodine solution.

[Note 1:--Potassium iodide usually contains small amounts of potassium

iodate as impurity which, when the iodide is brought into an acid

solution, liberates iodine, just as does the potassium bromate used as

a standard. It is necessary to determine the amount of thiosulphate

which reacts with the iodine thus liberated by making a "blank test"

with the iodide and acid alone. As the iodate is not always uniformly

distributed throughout the iodide, it is better to make up a

sufficient volume of a solution of the iodide for the purposes of the

work in hand, and to make the blank test by using the same volume of

the iodide solution as is added in the standardizing process. The

iodide solution should contain about 3 grams of the salt in 10 cc.]

[Note 2: The color of the iodo-starch is somewhat less satisfactory in

concentrated solutions of the alkali salts, notably the iodides. The

dilution prescribed obviates this difficulty.]

!Method B!

PROCEDURE.--Weigh out two portions of 0.25-0.27 gram of clean copper

wire into 250 cc. Erlenmeyer flasks (Note 1). Add to each 5 cc. of

concentrated nitric acid (sp. gr. 1.42) and 25 cc. of water, cover,

and warm until solution is complete. Add 5 cc. of bromine water and

boil until the excess of bromine is expelled. Cool, and add strong

ammonia (sp. gr. 0.90) drop by drop until a deep blue color indicates

the presence of an excess. Boil the solution until the deep blue is

replaced by a light bluish green, or a brown stain appears on the

sides of the flask (Note 2). Add 10 cc. of strong acetic acid (sp.

gr. 1.04), cool under the water tap, and add a solution of potassium

iodide (Note 3) containing about 3 grams of the salt, and titrate

with thiosulphate solution until the color of the liberated iodine

is nearly destroyed. Then add 1-2 cc. of freshly prepared starch

solution, and add thiosulphate solution, drop by drop, until the blue

color is discharged.

From the data obtained, including the "blank test" of the iodide,

calculate the relation of the thiosulphate solution to the normal.

[Note 1: While copper wire of commerce is not absolutely pure, the

requirements for its use as a conductor of electricity are such that

the impurities constitute only a few hundredths of one per cent and

are negligible for analytical purposes.]

[Note 2: Ammonia neutralizes the free nitric acid. It should be added

in slight excess only, since the excess must be removed by boiling,

which is tedious. If too much ammonia is present when acetic acid is

added, the resulting ammonium acetate is hydrolyzed, and the ammonium

hydroxide reacts with the iodine set free.]

[Note 3: A considerable excess of potassium iodide is necessary for

the prompt liberation of iodine. While a large excess will do no harm,

the cost of this reagent is so great that waste should be avoided.]

!Method C!

PROCEDURE.--Weigh out into 500 cc. beakers two portions of 0.175-0.200

gram each of pure arsenious oxide. Dissolve each of these in 10 cc. of

sodium hydroxide solution, with stirring. Dilute the solutions to 150

cc. and add dilute hydrochloric acid until the solutions contain a few

drops in excess, and finally add to each a concentrated solution of

5 grams of pure sodium bicarbonate (NaHCO\_{3}) in water. 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 by more than a

few drops (Note 1).

From the corrected volume of the iodine solution used to oxidize the

arsenious oxide, calculate its relation to the normal. From the

ratio between the solutions, calculate the similar value for the

thiosulphate solution.

[Note 1: Arsenious oxide dissolves more readily in caustic alkali than

in a bicarbonate solution, 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 neutral with the

solution of bicarbonate, part of which reacts with the acid, the

excess remaining in solution.

The reaction during titration is the following:

Na\_{3}AsO\_{3} + I\_{2} + 2NaHCO\_{3} --> Na\_{3}AsO\_{4} + 2NaI + 2CO\_{2}

+ H\_{2}O

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.]

DETERMINATION OF COPPER IN ORES

Copper ores vary widely in composition from the nearly pure copper

minerals, such as malachite and copper sulphide, to very low grade

materials which contain such impurities as silica, lead, iron, silver,

sulphur, arsenic, and antimony. In nearly all varieties there will be

found a siliceous residue insoluble in acids. The method here given,

which is a modification of that described by A.H. Low (!J. Am. Chem.

Soc.! (1902), 24, 1082), provides for the extraction of the copper

from commonly occurring ores, and for the presence of their common

impurities. For practice analyses it is advisable to select an ore of

a fair degree of purity.

PROCEDURE.-- Weigh out two portions of about 0.5 gram each of the

ore (which should be ground until no grit is detected) into 250 cc.

Erlenmeyer flasks or small beakers. Add 10 cc. of concentrated nitric

acid (sp. gr. 1.42) and heat very gently until the ore is decomposed

and the acid evaporated nearly to dryness (Note 1). Add 5 cc. of

concentrated hydrochloric acid (sp. gr. 1.2) and warm gently. Then

add about 7 cc. of concentrated sulphuric acid (sp. gr. 1.84) and

evaporate over a free flame until the sulphuric acid fumes freely

(Note 2). It has then displaced nitric and hydrochloric acid from

their compounds.

Cool the flask or beaker, add 25 cc. of water, heat the solution

to boiling, and boil for two minutes. Filter to remove insoluble

sulphates, silica and any silver that may have been precipitated as

silver chloride, and receive the filtrate in a small beaker, washing

the precipitate and filter paper with warm water until the filtrate

and washings amount to 75 cc. Bend a strip of aluminium foil (5 cm. x

12 cm.) into triangular form and place it on edge in the beaker. Cover

the beaker and boil the solution (being careful to avoid loss of

liquid by spattering) for ten minutes, but do not evaporate to small

volume.

Wash the cover glass and sides of the beaker. The copper should now be

in the form of a precipitate at the bottom of the beaker or adhering

loosely to the aluminium sheet. Remove the sheet, wash it carefully

with hydrogen sulphide water and place it in a small beaker. Decant

the solution through a filter, wash the precipitated copper twice by

decantation with hydrogen sulphide water, and finally transfer the

copper to the filter paper, where it is again washed thoroughly, being

careful at all times to keep the precipitated copper covered with the

wash water. Remove and discard the filtrate and place an Erlenmeyer

flask under the funnel. Pour 15 cc. of dilute nitric acid (sp. gr.

1.20) over the aluminium foil in the beaker, thus dissolving any

adhering copper. Wash the foil with hot water and remove it. Warm this

nitric acid solution and pour it slowly through the filter paper,

thereby dissolving the copper on the paper, receiving the acid

solution in the Erlenmeyer flask. Before washing the paper, pour 5 cc.

of saturated bromine water (Note 3) through it and finally wash the

paper carefully with hot water and transfer any particles of copper

which may be left on it to the Erlenmeyer flask. Boil to expel the

bromine. Add concentrated ammonia drop by drop until the appearance of

a deep blue coloration indicates an excess. Boil until the deep blue

is displaced by a light bluish green coloration, or until brown stains

form on the sides of the flask. Add 10 cc. of strong acetic acid (Note

4) and cool under the water tap. Add a solution containing about 3

grams of potassium iodide, as in the standardization, and titrate with

thiosulphate solution until the yellow of the liberated iodine is

nearly discharged. Add 1-2 cc. of freshly prepared starch solution and

titrate to the disappearance of the blue color.

From the data obtained, calculate the percentage of copper (Cu) in the

ore.

[Note 1: Nitric acid, because of its oxidizing power, is used as a

solvent for the sulphide ores. As a strong acid it will also dissolve

the copper from carbonate ores. The hydrochloric acid is added to

dissolve oxides of iron and to precipitate silver and lead. The

sulphuric acid displaces the other acids, leaving a solution

containing sulphates only. It also, by its dehydrating action, renders

silica from silicates insoluble.]

[Note 2: Unless proper precautions are taken to insure the correct

concentrations of acid the copper will not precipitate quantitatively

on the aluminium foil; hence care must be taken to follow directions

carefully at this point. Lead and silver have been almost completely

removed as sulphate and chloride respectively, or they too would

be precipitated on the aluminium. Bismuth, though precipitated on

aluminium, has no effect on the analysis. Arsenic and antimony

precipitate on aluminium and would interfere with the titration if

allowed to remain in the lower state of oxidation.]

[Note 3: Bromine is added to oxidize arsenious and antimonious

compounds from the original sample, and to oxidize nitrous acid formed

by the action of nitric acid on copper and copper sulphide.]

[Note 4: This reaction can be carried out in the presence of sulphuric

and hydrochloric acids as well as acetic acid, but in the presence

of these strong acids arsenic and antimonic acids may react with the

hydriodic acid produced with the liberation of free iodine, thereby

reversing the process and introducing an error.]

DETERMINATION OF ANTIMONY IN STIBNITE

Stibnite is native antimony sulphide. Nearly pure samples of this

mineral are easily obtainable and should be used for practice, since

many impurities, notably iron, seriously interfere with the accurate

determination of the antimony by iodometric methods. It is, moreover,

essential that the directions with respect to amounts of reagents

employed and concentration of solutions should be followed closely.

PROCEDURE.--Grind the mineral with great care, and weigh out two

portions of 0.35-0.40 gram into small, dry beakers (100 cc.).

Cover the beakers and pour over the stibnite 5 cc. of concentrated

hydrochloric acid (sp. gr. 1.20) and warm gently on the water bath

(Note 1). When the residue is white, add to each beaker 2 grams of

powdered tartaric acid (Note 2). 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 (Note

3).

If 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.

Carefully neutralize most of the acid with ammonium hydroxide solution

(sp. gr. 0.96), but leave it distinctly acid (Note 4). Dissolve 3

grams of sodium bicarbonate in 200 cc. of water in a 500 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 excess (Notes 5 and 6).

From the corrected volume of the iodine solution required to oxidize

the antimony, calculate the percentage of antimony (Sb) in the

stibnite.

[Note 1: Antimony chloride is volatile with steam from its

concentrated solutions; hence these solutions must not be boiled until

they have been diluted.]

[Note 2: Antimony salts, such as the chloride, are readily hydrolyzed,

and compounds such as 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.]

[Note 3: The action of hydrochloric acid upon the sulphide sets free

sulphureted hydrogen, a part of which is held in solution 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 the sulphureted hydrogen was all expelled on

solution of the stibnite.]

[Note 4: Ammonium hydroxide is added to neutralize most of the acid,

thus lessening the amount of sodium bicarbonate to be added. The

ammonia should not neutralize all of the acid.]

[Note 5: The reaction which takes place during titration may be

expressed thus:

Na\_{3}SbO\_{3} + 2NaHCO\_{3} + I\_{2} --> Na\_{3}SbO\_{4} + 2NaI + H\_{2}O +

2CO\_{2}.]

[Note 6: 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 very slight precipitation of an antimony

compound which is slowly acted upon by the iodine when the latter is

momentarily present 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.]

CHLORIMETRY

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\_{3}AsO\_{3} --> Na\_{3}AsO\_{4} + NaCl.

The sodium arsenite may be prepared from pure arsenious oxide,

as described below, and is stable for considerable periods; but

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 dilute hydrochloric

acid. Add 30 grams of sodium bicarbonate dissolved in a little water,

and dilute the solution to exactly 1000 cc. in a measuring flask.

Transfer the solution to a dry liter bottle and mix thoroughly.

It is possible to dissolve the arsenious oxide directly in a solution

of sodium bicarbonate, with gentle warming, but solution in sodium

hydroxide takes place much more rapidly, and the excess of the

hydroxide is readily neutralized by hydrochloric acid, with subsequent

addition of the bicarbonate to maintain neutrality during the

titration.

The indicator required for this process is made by dipping strips of

filter paper in a starch solution prepared as described on page 76,

to which 1 gram of potassium iodide has been added. These strips are

allowed to drain and spread upon a watch-glass until dry. 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.

DETERMINATION OF THE AVAILABLE CHLORINE IN BLEACHING POWDER

Bleaching powder consists mainly of a calcium compound which is a

derivative of both hydrochloric and hypochlorous acids. Its formula is

CaClOCl. Its use as a bleaching or disinfecting agent, or as a source

of chlorine, depends upon the amount of hypochlorous acid which it

yields when treated with a stronger acid. It is customary to express

the value of bleaching powder in terms of "available chlorine," by

which is meant the chlorine present as hypochlorite, but not the

chlorine present as chloride.

PROCEDURE.--Weigh out from a stoppered test tube into a porcelain

mortar about 3.5 grams of bleaching powder (Note 1). Triturate the

powder in the mortar with successive portions of water until it is

well ground and wash the contents into a 500 cc. measuring flask

(Note 2). Fill the flask to the mark with water and shake thoroughly.

Measure off 25 cc. of this semi-solution in a measuring flask, or

pipette, observing the precaution that the liquid removed shall

contain approximately its proportion of suspended matter.

Empty the flask or pipette 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. Repeat the titration, using a second 25 cc. portion.

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\_{4}O\_{6} + 4Cl\_{2} + 4H\_{2}O --> 2As\_{2}O\_{5} + 8HCl

Note that only one twentieth of the original weight of bleaching

powder enters into the reaction.

[Note 1: 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.]

[Note 2: Bleaching powder is easily acted upon by the carbonic acid in

the air, which liberates the weak hypochlorous acid. This, of course,

results in a loss of available chlorine. The original material for

analysis should be kept in a closed container and protected form the

air as far as possible. It is difficult to obtain analytical samples

which are accurately representative of a large quantity of the

bleaching powder. The procedure, as outlined, will yield results which

are sufficiently exact for technical purposes.]

III. PRECIPITATION METHODS

DETERMINATION OF SILVER BY THE THIOCYANATE PROCESS

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},

3KSCN + Fe(NO\_{3})\_{3} --> Fe(SCN)\_{3} + 3KNO\_{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 potassium thiocyanate should contain an amount

of the salt per liter of solution which would yield sufficient

(CNS)^{-} to combine with one gram of hydrogen to form HCNS, i.e.,

a gram-molecular weight of the salt or 97.17 grams. If the ammonium

thiocyanate is used, the amount is 76.08 grams. To prepare the

solution for this determination, which should be approximately 0.05

N, dissolve about 5 grams of potassium thiocyanate, or 4 grams of

ammonium thiocyanate, in a small amount of water; dilute this solution

to 1000 cc. in a liter bottle and mix as usual.

Prepare 20 cc. of a saturated solution of ferric alum and add 5 cc. of

dilute nitric acid (sp. gr. 1.20). About 5 cc. of this solution should

be used as an indicator.

STANDARDIZATION

PROCEDURE.--Crush a small quantity of silver nitrate crystals in a

mortar (Note 1). Transfer them to a watch-glass and dry them for an

hour at 110°C., protecting them from dust or other organic matter

(Note 2). Weigh out two portions of about 0.5 gram each and dissolve

them in 50 cc. of water. Add 10 cc. of dilute nitric acid which has

been recently boiled to expel the lower oxides of nitrogen, if any,

and then add 5 cc. of the indicator solution. Run in the thiocyanate

solution from a burette, with constant stirring, allowing the

precipitate to settle occasionally to obtain an exact recognition

of the end-point, until a faint red tinge can be detected in the

solution.

From the data obtained, calculate the relation of the thiocyanate

solution to the normal.

[Note 1: The thiocyanate cannot be accurately weighed; its solutions

must, therefore, be standardized against silver nitrate (or pure

silver), either in the form of a standard solution or in small,

weighed portions.]

[Note 2: 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.

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 end-point is lessened by setting

aside a small fraction of the silver solution, to be added near 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 dilute nitric acid (sp. gr. 1.2) and

boil until all the nitrous compounds are expelled (Note 1). Cool the

solution, dilute to 50 cc., and add 5 cc. of the indicator solution,

and titrate with the thiocyanate to the appearance of the faint red

coloration (Note 2).

From the corrected volume of the thiocyanate solution required,

calculate the percentage of silver in the coin.

[Note 1: The reaction with silver may be carried out in nitric acid

solutions 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, as these sometimes

cause a reddening of the indicator solution. All utensils, distilled

water, the nitric acid and the beakers must be free from chlorides,

as the presence of these will cause precipitation of silver chloride,

thereby introducing an error.]

[Note 2: The solution containing the silver precipitate, as well as

those from the standardization, should be placed in the receptacle for

"silver residues" as a matter of economy.]

PART III

GRAVIMETRIC ANALYSIS

GENERAL DIRECTIONS

Gravimetric analyses involve the following principal steps: first, the

weighing of the sample; second, the solution of the sample; third, the

separation of some substance from solution containing, or bearing a

definite relation to, the constituent to be measured, under conditions

which render this separation as complete as possible; and finally,

the segregation of that substance, commonly by filtration, and the

determination of its weight, or that of some stable product formed

from it on ignition. For example, the gravimetric determination of

aluminium is accomplished by solution of the sample, by precipitation

in the form of hydroxide, collection of the hydroxide upon a filter,

complete removal by washing of all foreign soluble matter, and the

burning of the filter and ignition of the precipitate to aluminium

oxide, in which condition it is weighed.

Among the operations which are common to nearly all gravimetric

analyses are precipitation, washing of precipitates, ignition of

precipitates, and the use of desiccators. In order to avoid burdensome

repetitions in the descriptions of the various gravimetric procedures

which follow, certain general instructions are introduced at this

point. These instructions must, therefore, be considered to be as much

a part of all subsequent procedures as the description of apparatus,

reagents, or manipulations.

The analytical balance, the fundamentally important instrument in

gravimetric analysis, has already been described on pages 11 to 15.

PRECIPITATION

For successful quantitative precipitations those substances are

selected which are least soluble under conditions which can be easily

established, and which separate from solution in such a state that

they can be filtered readily and washed free from admixed material.

In general, the substances selected are the same as those already

familiar to the student of Qualitative Analysis.

When possible, substances are selected which separate in crystalline

form, since such substances are less likely to clog the pores of

filter paper and can be most quickly washed. In order to increase the

size of the crystals, which further promotes filtration and washing,

it is often desirable to allow a precipitate to remain for some time

in contact with the solution from which it has separated. The solution

is often kept warm during this period of "digestion." The small

crystals gradually disappear and the larger crystals increase in size,

probably as the result of the force known as surface tension, which

tends to reduce the surface of a given mass of material to a minimum,

combined with a very slightly greater solubility of small crystals as

compared with the larger ones.

Amorphous substances, such as ferric hydroxide, aluminium hydroxide,

or silicic acid, separate in a gelatinous form and are relatively

difficult to filter and wash. Substances of this class also exhibit

a tendency to form, with pure water, what are known as colloidal

solutions. To prevent this as far as possible, they are washed with

solutions of volatile salts, as will be described in some of the

following procedures.

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.

FUNNELS AND FILTERS

Filtration in analytical processes is most commonly effected through

paper filters. In special cases these may be advantageously replaced

by an asbestos filter in a perforated porcelain or platinum crucible,

commonly known, from its originator, as a "Gooch filter." The

operation and use of a filter of this type is described on page 103.

Porous crucibles of a material known as alundum may also be employed

to advantage in special cases.

The glass funnels selected for use with paper filters should have an

angle as near 60° as possible, and a narrow stem about six inches in

length. The filters employed should be washed filters, i.e., those

which have been treated with hydrochloric and hydrofluoric acids, and

which on incineration leave a very small and definitely known weight

of ash, generally about .00003 gram. Such filters are readily

obtainable on the market.

The filter should be carefully folded to fit the funnel according to

either of the two well-established methods described in the Appendix.

It should always be placed so that the upper edge of the paper

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 stem completely, forming a continuous

column of liquid which, by its hydrostatic pressure, produces a gentle

suction, thus materially promoting the rapidity of filtration. Unless

the filter allows free passage of water under these conditions, it is

likely to give much trouble when a precipitate is placed upon it.

The use of a suction pump to promote filtration is rarely altogether

advantageous in quantitative analysis, if paper filters are employed.

The tendency of the filter to break, unless the point of the filter

paper is supported by a perforated porcelain cone or a small "hardened

filter" of parchment, and the tendency of the precipitates to pass

through the pores of the filter, more than compensate for the possible

gain in time. On the other hand, filtration by suction may be useful

in the case of precipitates which do not require ignition before

weighing, or in the case of precipitates which are to be discarded

without weighing. This is best accomplished with the aid of the

special apparatus called a Gooch filter referred to above.

FILTRATION AND WASHING OF PRECIPITATES

Solutions should be filtered while hot, as far as possible, since

the passage of a 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.

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 smaller number of washings 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 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

ultimately becomes necessary to transfer it to the filter and complete

the washing there.

A precipitate should never completely fill a filter. 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.

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.

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 tested to assure complete removal of foreign material. 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 common 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.

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 soft rubber device sometimes called a "policeman."

DESICCATORS

Desiccators should be filled with fused, anhydrous calcium chloride,

over which is placed a clay triangle, or an iron triangle covered with

silica tubes, to support the crucible or other utensils. The cover of

the desiccator should be made air-tight by the use of a thin coating

of vaseline.

Pumice moistened with concentrated 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 practically efficient and does not slop

about when the desiccator is moved.

Desiccators should never remain uncovered for any length of time. The

dehydrating agents rapidly lose their efficiency on exposure to the

air.

CRUCIBLES

It is often necessary in quantitative analysis to employ fluxes to

bring into solution substances which are not dissolved by acids. The

fluxes in most common use are sodium carbonate and sodium or potassium

acid sulphate. In gravimetric analysis it is usually necessary to

ignite the separated substance after filtration and washing, in order

to remove moisture, or to convert it through physical or chemical

changes into some definite and stable form for weighing. Crucibles

to be used in fusion processes must be made of materials which will

withstand the action of the fluxes employed, and crucibles to be used

for ignitions must be made of material which will not undergo any

permanent change during the ignition, since the initial weight of the

crucible must be deducted from the final weight of the crucible and

product to obtain the weight of the ignited substance. The three

materials which satisfy these conditions, in general, are platinum,

porcelain, and silica.

Platinum crucibles have the advantage that they can be employed at

high temperatures, but, on the other hand, these crucibles can never

be used when there is a possibility of the reduction to the metallic

state of metals like lead, copper, silver, or gold, which would alloy

with and ruin the crucible. When platinum crucibles are used with

compounds of arsenic or phosphorus, special precautions are necessary

to prevent damage. This statement applies to both fusions and

ignitions.

Fusions with sodium carbonate can be made only in platinum, since

porcelain or silica crucibles are attacked by this reagent. Acid

sulphate fusions, which require comparatively low temperatures, can

sometimes be made in platinum, although platinum is slightly attacked

by the flux. Porcelain or silica crucibles may be used with acid

fluxes.

Silica crucibles are less likely to crack on heating than porcelain

crucibles on account of their smaller coefficient of expansion.

Ignition of substances not requiring too high a temperature may be

made in porcelain or silica crucibles.

Iron, nickel or silver crucibles are used in special cases.

In general, platinum crucibles should be used whenever such use is

practicable, and this is the custom in private, research or commercial

laboratories. Platinum has, however, become so valuable that it is

liable to theft unless constantly under the protection of the user. As

constant protection is often difficult in instructional laboratories,

it is advisable, in order to avoid serious monetary losses, to use

porcelain or silica crucibles whenever these will give satisfactory

service. When platinum utensils are used the danger of theft should

always be kept in mind.

PREPARATION OF CRUCIBLES FOR USE

All crucibles, of whatever material, must always be cleaned, ignited

and allowed to cool in a desiccator before weighing, since all bodies

exposed to the air condense on their surfaces a layer of moisture

which increases their weight. The amount and weight of this moisture

varies with the humidity of the atmosphere, and the latter may change

from hour to hour. The air in the desiccator (see above) is kept at

a constant and low humidity by the drying agent which it contains.

Bodies which remain in a desiccator for a sufficient time (usually

20-30 minutes) retain, therefore, on their surfaces a constant weight

of moisture which is the same day after day, thus insuring constant

conditions.

Hot objects, such as ignited crucibles, should be allowed to cool in

the air until, when held near the skin, but little heat is noticeable.

If this precaution is not taken, the air within the desiccator is

strongly heated and expands before the desiccator is covered. As the

temperature falls, the air contracts, causing a reduction of air

pressure within the covered vessel. When the cover is removed (which

is often rendered difficult) the inrush of air from the outside may

sweep light particles out of a crucible, thus ruining an entire

analysis.

Constant heating of platinum causes a slight crystallization of the

surface which, if not removed, penetrates into the crucible. Gentle

polishing of the surface destroys the crystalline structure and

prevents further damage. If sea sand is used for this purpose, 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 in use may often be cleaned by the fusion

in them of potassium or sodium 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 sulphates sometimes expand so rapidly on cooling as to split

the crucible. The fused material should be poured out, while hot, on

to a !dry! tile or iron surface.

IGNITION OF PRECIPITATES

Most 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 often requires more care

during ignition than a thoroughly moist one.

The details of the ignition of precipitates vary so much with the

character of the precipitate, its moisture content, and temperature to

which it is to be heated, that these details will be given under the

various procedures which follow.

DETERMINATION OF CHLORINE IN SODIUM CHLORIDE

!Method A. With the Use of a Gooch Filter!

PROCEDURE.--Carefully clean a 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 (see Appendix). Hold the tube over the top of a beaker

(200-300 cc.), 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 dilute nitric acid

(sp. gr. 1.20) (Note 2). 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 (Note 3). This heating should not take place in direct sunlight

(Note 4). 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. If a precipitate, or cloudiness, appears as the drops fall

into the solution, heat again, and stir until the whole precipitate

has coagulated. The solution is then ready for filtration.

Prepare a Gooch filter as follows: Fold over the top of a Gooch funnel

(Fig. 2) a piece of rubber-band tubing, such as is known as "bill-tie"

tubing, and fit into the mouth of the funnel a perforated porcelain

crucible (Gooch crucible), making sure that when the crucible is

gently forced into the mouth of the funnel an airtight joint results.

(A small 1 or 1-1/4-inch glass funnel may be used, in which case the

rubber tubing is stretched over the top of the funnel and then drawn

up over the side of the crucible until an air-tight joint is secured.)

[ILLUSTRATION: FIG. 2]

Fit the funnel into the stopper of a filter bottle, and connect the

filter bottle with the suction pump. Suspend some finely divided

asbestos, which has been washed with acid, in 20 to 30 cc. of water

(Note 1); 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 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 and hold it in place by pouring a

very thin layer of asbestos over it, washing the whole carefully;

then place the crucible in a small beaker, and place both in a drying

closet at 100-110°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.

Place 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 onto a Gooch filter hold the

stirring-rod at first well down in the crucible, so that the liquid

does not fall with any force upon the asbestos, and afterward keep the

crucible will filled with the solution.

Pour the liquid above the silver chloride slowly onto the filter,

leaving the precipitate in the beaker as far as possible. Wash the

precipitate twice by decantation with warm water; then transfer it

to the filter with the aid of a stirring-rod with a rubber tip and a

stream from the wash-bottle.

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.

Finally, wash the precipitate thoroughly with warm water until free

from soluble silver salts. To test the washings, disconnect the

suction at the flask and remove the funnel or filter tube from the

suction flask. Hold the end of the tube over the mouth of a small test

tube and add from a wash-bottle 2-3 cc. of water. Allow the water to

drip through into the test tube and add a drop of dilute hydrochloric

acid. No precipitate or cloud should form in the wash-water (Note 16).

Dry the filter and contents at 100-110°C. until the weight is constant

within 0.0003 gram, as described for the preparation of the filter.

Deduct the weight of the dry crucible from the final weight, and from

the weight of silver chloride thus obtained calculate the percentage

of chlorine in the sample of sodium chloride.

[Note 1: The washed asbestos for this type of filter is prepared by

digesting in concentrated hydrochloric acid, long-fibered asbestos

which has been cut in pieces of about 0.5 cm. in length. After

digestion, the asbestos is filtered off on a filter plate and washed

with hot, distilled water until free from chlorides. A small portion

of the asbestos is shaken with water, forming a thin suspension, which

is bottled and kept for use.]

[Note 2: 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.]

[Note 3: 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

coagulates and settles.]

[Note 4: The precipitate should not be exposed to strong sunlight,

since under those conditions a reduction of the silver chloride ensues

which is accompanied by a loss of chlorine. The superficial alteration

which the chloride undergoes in diffused daylight is not sufficient

to materially affect the accuracy of the determination. It should be

noted, however, that a slight error does result from the effect of

light upon the silver chloride precipitate and in cases in which the

greatest obtainable accuracy is required, the procedure described

under "Method B" should be followed, in which this slight reduction of

the silver chloride is corrected by subsequent treatment with nitric

and hydrochloric acids.]

[Note 5: The asbestos used in the Gooch filter should be of the finest

quality and capable of division into minute fibrous particles. A

coarse felt is not satisfactory.]

[Note 6: The precipitate must be washed with warm water until it is

absolutely free from silver and sodium nitrates. It may be assumed

that the sodium salt is 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.

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. The chloride is also somewhat soluble in solutions of

many chlorides, in solutions of silver nitrate, and in concentrated

nitric acid.

As a matter of economy, the filtrate, which contains whatever silver

nitrate was added in excess, may be set aside. The silver can be

precipitated as chloride and later converted into silver nitrate.]

[Note 7: 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.]

!Method B. With the Use of a Paper Filter!

PROCEDURE.--Weigh out two portions of sodium chloride of about

0.25-0.3 gram each and proceed with the precipitation of the silver

chloride as described under Method A above. When the chloride is ready

for filtration prepare two 9 cm. washed paper filters (see Appendix).

Pour the liquid above the precipitates through the filters, wash twice

by decantation and transfer the precipitates to the filters, finally

washing them until free from silver solution as described. The funnel

should then be covered with a moistened filter paper by stretching it

over the top and edges, 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 (Note 1). 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 from the

air. Fold the filter paper carefully, roll it into a small cone, and

wind loosely around !the top! a piece of small platinum wire (Note 2).

Hold the filter by the wire over a small 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 a low

flame well at its base, until all the carbon of the filter has been

consumed. Allow the crucible to cool, add two drops of concentrated

nitric acid and one drop of concentrated 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 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 concentrated nitric acid and

one drop of concentrated hydrochloric acid, and again heat with great

caution until the acids are expelled and the precipitate is white,

when the temperature is slowly raised until the silver chloride just

begins to fuse at the edges (Note 3). 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

percentage of chlorine in the sample of sodium chloride taken for

analysis.

[Note 1: 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 difficulty. The small amount of

silver reduced from the chloride adhering to the filter paper after

separating the bulk of the precipitate, and igniting the paper

as prescribed, can be dissolved in nitric acid, and completely

reconverted to chloride by hydrochloric acid. The subsequent addition

of the two acids to the main portion of the precipitate restores the

chlorine to any chloride which may have been partially reduced by the

sunlight. The excess of the acids is volatilized by heating.]

[Note 2: 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 were placed nearer the

apex, such contact could hardly be avoided.]

[Note 3: 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.]

DETERMINATION OF IRON AND OF SULPHUR IN FERROUS AMMONIUM SULPHATE,

FESO\_{4}.(NH\_{4})\_{2}SO\_{4}.6H\_{2}O

DETERMINATION OF IRON

PROCEDURE.--Weigh out into beakers (200-250 cc.) two portions of the

sample (Note 1) of about 1 gram each and dissolve these in 50 cc. of

water, to which 1 cc. of dilute hydrochloric acid (sp. gr. 1.12) has

been added (Note 2). Heat the solution to boiling, and while at the

boiling point add concentrated 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 (Note 3). 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 hydrochloric and nitric acids added (see Appendix for

data), and also to precipitate the iron as ferric hydroxide from the

weight of the ferrous ammonium sulphate taken for analysis, assuming

it to be pure (Note 4). The volume thus calculated will be in excess

of that actually required for precipitation, 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

twice by decantation with 100 cc. of hot water. Reserve the filtrate.

Dissolve the iron from the filter with hot, dilute hydrochloric acid

(sp. gr. 1.12), adding it in small portions, using as little as

possible and noting the volume used. 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 a

calculated excess of ammonia.

Wash the precipitate twice by decantation, and finally transfer it to

the original filter. Wash continuously with hot water until finally

3 cc. of the washings, acidified with nitric acid (Note 5), show

no evidences of the presence of chlorides when tested with silver

nitrate. The filtrate and washings are combined with those from the

first precipitation and treated for the determination of sulphur, as

prescribed on page 112.

[Note 1: If a selection of pure material for analysis is to be made,

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 material is desired, it is preferable to grind the

whole together, mix thoroughly, and take a sample from the mixture for

analysis.]

[Note 2: When aqueous solutions of ferrous compounds are heated in the

air, oxidation of the Fe^{++} ions to Fe^{+++} ions readily occurs in

the absence of free acid. The H^{+} and OH^{-} ions from water are

involved in the oxidation process and the result is, in effect, the

formation of some ferric hydroxide which tends to separate. Moreover,

at the boiling temperature, the ferric sulphate produced by the

oxidation hydrolyzes in part with the formation of a basic ferric

sulphate, which also tends to separate from solution. The addition of

the hydrochloric acid prevents the formation of ferric hydroxide, and

so far reduces the ionization of the water that the hydrolysis of the

ferric sulphate is also prevented, and no precipitation occurs on

heating.]

[Note 3: The nitric acid, after attaining a moderate strength,

oxidizes the Fe^{++} ions to Fe^{+++} ions with the formation of an

intermediate nitroso-compound 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

compounds. A drop of the oxidized solution should be tested on

a watch-glass with potassium ferricyanide, to insure a complete

oxidation. 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\_{2}O + 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\_{2}O,

assuming that only enough nitric acid is added to complete the

oxidation.]

[Note 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.

A gradual neutralization with ammonia would result in the local

formation of a neutral solution within the liquid, and subsequent

deposition of a basic sulphate as a consequence of a local deficiency

of OH^{-} ions from the NH\_{4}OH and a partial hydrolysis of the

ferric salt. Even with this precaution the entire absence of sulphates

from the first iron precipitate 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 subsequent

precipitation with ammonia. The nitric acid is added to reoxidize this

iron.

To avoid errors arising from the solvent action of ammoniacal

liquids upon glass, the iron precipitate should be filtered without

unnecessary delay.]

[Note 5: The washings from the ferric hydroxide 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.]

!Ignition of the Iron Precipitate!

Heat a platinum or porcelain crucible, cool it in a desiccator and

weigh, repeating until a constant weight is obtained.

Fold the top of the filter paper over the moist precipitate of ferric

hydroxide and transfer it cautiously to the crucible. Wipe the inside

of the funnel with a small fragment of washed filter paper, if

necessary, and place the paper in the crucible.

Incline the crucible on its side, on a triangle supported on a

ring-stand, and stand the cover on edge at the mouth of the crucible.

Place a burner below the front edge of the crucible, using a low flame

and protecting it from drafts of air by means of a chimney. The heat

from the burner is thus reflected into the crucible and dries

the precipitate without danger of loss as the result of a sudden

generation of steam within the mass of ferric hydroxide. As the drying

progresses the burner may be gradually moved toward the base of the

crucible and the flame increased until the paper of the filter begins

to char and finally to smoke, as the volatile matter is expelled. This

is known as "smoking off" a filter, and the temperature should not be

raised sufficiently high during this process to cause the paper to

ignite, as the air currents produced by the flame of the blazing paper

may carry away particles of the precipitate.

When the paper is fully charred, move the burner to the base of the

crucible and raise the temperature to the full heat of the burner for

fifteen minutes, with the crucible still inclined on its side, but

without the cover (Note 1). Finally set the crucible upright in the

triangle, cover it, and heat at the full temperature of a blast lamp

or other high temperature burner. Cool and weigh in the usual manner

(Note 2). Repeat the strong heating until the weight is constant

within 0.0003 gram.

From the weight of ferric oxide (Fe\_{2}O\_{3}) calculate the percentage

of iron (Fe) in the sample (Note 3).

[Note 1: These directions for the ignition of the precipitate 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\_{3}O\_{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.]

[Note 2: 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.]

[Note 3: 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, from a quantitative

standpoint, other than those mentioned, are the following: All are

precipitable 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. The precipitation of the hydroxides

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.

The hydroxides yield on ignition an oxide suitable for weighing

(Al\_{2}O\_{3}, Cr\_{2}O\_{3}, Fe\_{2}O\_{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 dilute hydrochloric acid (sp. gr. 1.12) in moderate excess

and evaporate to dryness on the water bath. Add 10 cc. of concentrated

hydrochloric acid (sp. gr. 1.20) 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. beaker, dilute to about 400 cc., and

cautiously add hydrochloric acid until the solution shows a distinctly

acid reaction (Note 1). Heat the solution to boiling, and add !very

slowly! and with constant stirring, 20 cc. in excess of the calculated

amount of a hot barium chloride solution, containing about 20 grams

BaCl\_{2}.2H\_{2}O per liter (Notes 2 and 3). Continue the boiling for

about two minutes, allow the precipitate to settle, and decant the

liquid at the end of half an hour (Note 4). 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, testing the washings

as described in the determination of iron. The filter is then

transferred to a platinum or porcelain crucible and ignited, as

described above, until the weight is constant (Note 5). From the

weight of barium sulphate (BaSO\_{4}) obtained, calculate the

percentage of sulphur (S) in the sample.

[Note 1: 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 because of 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.]

[Note 2: 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:

(!Conc'n Ba^{++} x Conc'n SO\_{4}^{--})/(Conc'n BaSO\_{4}) = Const.!,

and since !Conc'n BaSO\_{4}! for the saturated solution has a constant

value (which is very small), it may be eliminated, when the expression

becomes !Conc'n Ba^{++} x 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 successful 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.]

[Note 3: Barium sulphate, in a larger measure than most compounds,

tends to carry down other substances which are present in the solution

from which it separates, even when these other substances are

relatively soluble, and 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 Kuster and Thiel (!Zeit. 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 (!Zeit. 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 anhydride upon ignition, causing low results, even

though the precipitate contains iron.

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.]

[Note 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 already noted, 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,

if practicable, to promote ease of filtration. The filtrate and

washings should 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 filtrate a gentle rotary motion,

when the sulphate, if present, will collect at the center of the

bottom of the beaker.]

[Note 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.]

[Note 6: 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 SULPHUR IN BARIUM SULPHATE

PROCEDURE.--Weigh out, into platinum crucibles, two portions of about

0.5 gram of the sulphate. Mix each in the crucible with five to six

times its weight of anhydrous 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. Remove the burner, and tip the crucible until the fused mass

flows nearly to its mouth. Hold it in that position until the mass has

solidified. When cold, the material may usually be detached in a lump

by tapping the crucible or gently pressing it near its upper edge. 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 and placed 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 (Note 1). Pour over the residue 20 cc. of a solution of

sodium carbonate and 10 cc. of water and heat to gentle boiling for

about three minutes (Note 2). 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 slowly add hot barium chloride solution, as in the preceding

determination. Add also any tests from the washings in which

precipitates have appeared. Filter, wash, ignite, and weigh.

From the weight of barium sulphate, calculate the percentage of

sulphur (S) in the sample.

[Note 1: This alkaline fusion is much employed to disintegrate

substances ordinarily insoluble in acids into two components, one

of which is water soluble and the other acid soluble. The reaction

involved is:

BaSO\_{4} + Na\_{2}CO\_{3}, --> BaCO\_{3}, + Na\_{2}SO\_{4}.

As the sodium sulphate is soluble in water, and the barium carbonate

insoluble, a separation between them is possible and the sulphur can

be determined in the water-soluble portion.

It should be noted that this method can be applied to the purification

of a precipitate of barium sulphate if contaminated by most of the

substances mentioned in Note 3 on page 114. The impurities pass into

the water solution together with the sodium sulphate, but, being

present in such minute amounts, do not again precipitate with the

barium sulphate.]

[Note 2: The barium carbonate is boiled with sodium carbonate solution

before filtration because the reaction 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).]

DETERMINATION OF PHOSPHORIC ANHYDRIDE IN APATITE

The mineral apatite is composed of calcium phosphate, associated with

calcium chloride, or fluoride. Specimens are easily obtainable which

are nearly pure and leave on treatment with acid only a slight

siliceous residue.

For the purpose of gravimetric determination, phosphoric acid is

usually precipitated from ammoniacal solutions in the form of

magnesium ammonium phosphate which, on ignition, is converted into

magnesium pyrophosphate. Since the calcium phosphate of the apatite

is also insoluble in ammoniacal solutions, this procedure cannot be

applied directly. The separation of the phosphoric acid from the

calcium must first be accomplished by precipitation in the form of

ammonium phosphomolybdate in nitric acid solution, using ammonium

molybdate as the precipitant. The "yellow precipitate," as it is often

called, is not always of a definite composition, and therefore not

suitable for direct weighing, but may be dissolved in ammonia, and the

phosphoric acid thrown out as magnesium ammonium phosphate from the

solution.

Of the substances likely to occur in apatite, silicic acid alone

interferes with the precipitation of the phosphoric acid in nitric

acid solution.

PRECIPITATION OF AMMONIUM PHOSPHOMOLYBDATE

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 (Note 1) into two beakers

of about 200 cc. capacity. Pour over them 20 cc. of dilute nitric acid

(sp. gr. 1.2) and warm gently until solvent action has apparently

ceased. Evaporate the solution cautiously to dryness, heat the residue

for about an hour at 100-110°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 (Note 2). Receive the filtrate in a beaker (200-500 cc.).

Test the washings with ammonia for calcium phosphate, but add all such

tests in which a precipitate appears to the original nitrate (Note 3).

The filtrate and washings must be kept as small as possible and should

not exceed 100 cc. in volume. Add aqueous ammonia (sp. gr. 0.96) 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 (Note 4). Warm the solution until it

cannot be comfortably held in the hand (about 60°C.) and, after

removal of the burner, add 75 cc. of ammonium molybdate solution which

has been !gently! warmed, but which must be perfectly clear. Allow

the mixture to stand at a temperature of about 50 or 60°C. for twelve

hours (Notes 5 and 6). 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 (Note 3).

[Footnote 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 nitrate, and leave it for

a few hours. It should then be carefully examined for a !yellow!

precipitate; a white precipitate may be neglected.

[Note 1: Magnesium ammonium phosphate, as noted below, is slightly

soluble under the conditions of operation. Consequently 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 unavoidable 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 phosphomolybdate

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.]

[Note 2: Soluble silicic acid would, if present, partially separate

with the phosphomolybdate, although not in combination with

molybdenum. Its previous removal by dehydration is therefore

necessary.]

[Note 3: When washing the siliceous residue the filtrate may be tested

for calcium by adding ammonia, 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.]

[Note 4: An excess of nitric acid exerts a slight solvent

action, while ammonium nitrate lessens the solubility; hence the

neutralization of the former by ammonia.]

[Note 5: The precipitation of the phosphomolybdate 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, but the filtrate should be tested

as in all quantitative procedures.

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 precipitate.]

[Note 6: The composition of the "yellow precipitate" undoubtedly

varies slightly with varying conditions at the time of its formation.

Its composition may probably fairly be represented by the formula,

(NH\_{4})\_{3}PO\_{4}.12MoO\_{3}.H\_{2}O, when precipitated under the

conditions prescribed in the procedure. Whatever other variations may

occur in its composition, the ratio of 12 MoO\_{3}:1 P 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. In principle, the procedure is comparable with that

described for the determination of iron by permanganate.]

PRECIPITATION OF MAGNESIUM AMMONIUM PHOSPHATE

PROCEDURE.--Dissolve the precipitate of phosphomolybdate upon the

filter by pouring through it dilute aqueous ammonia (one volume of

dilute ammonia (sp. gr. 0.96) and three volumes of water, which

should be carefully measured), and receive the solution in the beaker

containing the bulk of the precipitate. The total volume of nitrate

and washings should not much exceed 100 cc. Acidify the solution with

dilute hydrochloric acid, and heat it nearly to boiling. Calculate the

volume of magnesium ammonium chloride solution ("magnesia mixture")

required to precipitate the phosphoric acid, assuming 40 per cent

P\_{2}O\_{5} in the apatite. Measure out about 5 cc. in excess of this

amount, and pour it into the acid solution. Then add slowly dilute

ammonium hydroxide (1 volume of strong ammonia (sp. gr. 0.90) and 9

volumes of water), stirring constantly until a precipitate forms. Then

add a volume of filtered, concentrated ammonia (sp. gr. 0.90) equal to

one third of the volume of liquid in the beaker (Note 1). Allow the

whole to cool. The precipitated magnesium ammonium phosphate should

then be definitely crystalline in appearance (Note 2). (If it is

desired to hasten the precipitation, the solution may be cooled, first

in cold and then in ice-water, and stirred !constantly! for half an

hour, when precipitation will usually be complete.)

Decant the clear liquid through a filter, and transfer the precipitate

to the filter, using as wash-water a mixture of one volume of

concentrated ammonia and three volumes of water. It is not necessary

to clean the beaker completely or to wash the precipitate thoroughly

at this point, as it is necessary to purify it by reprecipitation.

[Note 1: 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

concentrated aqueous ammonia (sp. gr. 0.90) 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.

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 tendency

of the magnesium precipitate to carry down molybdic acid is also

increased 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.]

[Note 2: 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.]

REPRECIPITATION AND IGNITION OF MAGNESIUM AMMONIUM PHOSPHATE

A single precipitation of the magnesium compound in the presence of

molybdenum compounds rarely yields a pure product. The molybdenum can

be removed by solution of the precipitate in acid and precipitation

of the molybdenum by sulphureted hydrogen, after which the magnesium

precipitate may be again thrown down. It is usually more satisfactory

to dissolve the magnesium precipitate and reprecipitate the phosphate

as magnesium ammonium phosphate as described below.

PROCEDURE.--Dissolve the precipitate from the filter in a little

dilute hydrochloric acid (sp. gr. 1.12), allowing the acid solution to

run into the beaker in which the original precipitation was made (Note

1). 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 dilute

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 strong ammonia (sp. gr.

0.90), 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.

Transfer the moist precipitate to a weighed porcelain or platinum

crucible and ignite, using great care to raise the temperature slowly

while drying the filter in the crucible, and to insure the ready

access 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 the crucible, if of

platinum, and the 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.

If the ignited precipitate is persistently discolored by particles of

unburned carbon, moisten the mass with a drop or two of concentrated

nitric acid and heat cautiously, finally igniting strongly. The

acid will dissolve magnesium pyrophosphate from the surface of the

particles of carbon, which will then burn away. Nitric acid also aids

as an oxidizing agent in supplying oxygen for the combustion of the

carbon.

From the weight of magnesium pyrophosphate (Mg\_{2}P\_{2}O\_{7})

obtained, calculate the phosphoric anhydride (P\_{2}O\_{5}) in the

sample of apatite.

[Note 1: The ionic change involved in the precipitation of the

magnesium compound is

PO\_{4}^{---} + NH\_{4}^{+} + Mg^{++} --> [MgNH\_{4}PO\_{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\_{2}PO\_{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 magnesium 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.]

[Note 2: During ignition the magnesium ammonium phosphate loses

ammonia and water and is converted into magnesium pyrophosphate:

2MgNH\_{4}PO\_{4} --> Mg\_{2}P\_{2}O\_{7} + 2NH\_{3} + H\_{2}O.

The precautions mentioned on pages 111 and 123 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 a platinum crucible,

and the determination is valueless.]

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 variable proportions.

Many other minerals may be inclosed in limestones in small quantities,

and an exact qualitative analysis will often show the presence of

sulphides or sulphates, phosphates, and titanates, and the alkali or

even the heavy metals. No attempt is made in the following procedures

to provide a complete quantitative scheme which would take into

account all of these constituents. Such a scheme for a complete

analysis of a limestone may be found in Bulletin No. 700 of the United

States Geological Survey. It is assumed that, for these practice

determinations, a limestone is selected which contains only the more

common constituents first enumerated above.

DETERMINATION OF MOISTURE

The determination of the amount of moisture in minerals or ores is

often of great importance. Ores which have been exposed to the weather

during shipment may have absorbed enough moisture to appreciably

affect the results of analysis. Since it is essential that the seller

and buyer should make their analyses upon comparable material, it is

customary for each analyst to determine the moisture in the sample

examined, and then to calculate the percentages of the various

constituents with reference to a sample dried in the air, or at a

temperature a little above 100°C., which, unless the ore has undergone

chemical change because of the wetting, should be the same before and

after shipment.

PROCEDURE.--Spread 25 grams of the powdered sample on a weighed

watch-glass; weigh to the nearest 10 milligrams only and heat at

105°C.; weigh at intervals of an hour, after cooling in a desiccator,

until the loss of weight after an hour's heating does not exceed

10 milligrams. It should be noted that a variation in weight of 10

milligrams in a total weight of 25 grams is no greater relatively than

a variation of 0.1 milligram when the sample taken weighs 0.25 gram

DETERMINATION OF THE INSOLUBLE MATTER AND SILICA

PROCEDURE.--Weigh out two portions of the original powdered sample

(not the dried sample), of about 5 grams each, into 250 cc.

casseroles, and cover each with a watch-glass (Note 1). Pour over the

powder 25 cc. of water, and then add 50 cc. of dilute hydrochloric

acid (sp. gr. 1.12) in small portions, warming gently, until nothing

further appears to dissolve (Note 2). Evaporate to dryness on the

water bath. Pour over the residue a mixture of 5 cc. of water and

5 cc. of concentrated hydrochloric acid (sp. gr. 1.2) and again

evaporate to dryness, and finally heat for at least an hour at

a temperature of 110°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 hydrochloric acid, and then with hot water until

free from chlorides. Transfer the filter and contents to a porcelain

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 (Note 3).

Calculate the combined percentage of these in the limestone.

[Note 1: The relatively large weight (5 grams) 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.]

[Note 2: 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.]

[Note 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 converted by evaporation to dryness, and heating, into white,

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 insoluble

basic iron or aluminium salts on the filter when washing with hot

water.

If 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 151 should be followed. The filtrate from the silica is

then added to the main filtrate from the insoluble residue.]

DETERMINATION OF FERRIC OXIDE AND ALUMINIUM OXIDE (WITH MANGANESE)

PROCEDURE.--To the filtrate from the insoluble residue add ammonium

hydroxide until the solution just smells distinctly of ammonia, but do

not add an excess. Then add 5 cc. of saturated bromine water (Note 1),

and boil for five minutes. If the smell of ammonia has disappeared,

again add ammonium hydroxide in slight excess, and 3 cc. of bromine

water, and heat again for a few minutes. Finally add 10 cc. of

ammonium chloride solution and keep the solution warm until it barely

smells of ammonia; then filter promptly (Note 2). Wash the filter

twice with hot water, then (after replacing the receiving beaker) pour

through it 25 cc. of hot, dilute hydrochloric acid (one volume dilute

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 precipitation.

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 110. The residue after ignition consists of ferric

oxide, alumina, and mangano-manganic oxide (Mn\_{3}O\_{4}), if manganese

is present. These are commonly determined together (Note 3).

Calculate the percentage of the combined oxides in the limestone.

[Note 1: The addition of bromine water to the ammoniacal solutions

serves to oxidize any ferrous hydroxide to ferric hydroxide and to

precipitate manganese as MnO(OH)\_{2}. The solution must contain not

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.

The solution should not be strongly ammoniacal when the bromine is

added, as strong ammonia reacts with the bromine, with the evolution

of nitrogen.]

[Note 2: 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, this reprecipitation may be omitted.]

[Note 3: 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 66.

The aluminium is then determined by difference, after subtracting the

weight of ferric oxide corresponding to the amount of iron found.

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, Fay, !Quantitative Analyses!, First Edition, pp. 15-19 and

23-27).]

DETERMINATION OF CALCIUM

PROCEDURE.--To the combined filtrates from the double precipitation of

the hydroxides just described, add 5 cc. of dilute ammonium hydroxide

(sp. gr. 0.96), and transfer the liquid to a 500 cc. graduated flask,

washing out the beaker carefully. 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. Measure off one fifth of this

solution as follows (Note 1): 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 (400-500 cc.). Wash out the flask with

small quantities of water until it is clean, adding these to the 100

cc. of solution. When the duplicate portion of 100 cc. is measured out

from the solution, remember that the flask must be rinsed out twice

with that solution, as prescribed above, before the measurement is

made. (A 100 cc. pipette may be used to measure out the aliquot

portions, if preferred.)

Dilute each of the measured portions to 250 cc. with distilled water,

heat the whole 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 (Note 2); see that it is properly

labeled and reserve it to be combined with the filtrate from the

second calcium oxalate precipitation (Notes 3 and 4).

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 (Note 5) 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 with hydrochloric acid and combined with the

filtrate from the first precipitation. Begin at once the evaporation

of the solutions for the determination of magnesium as described

below.

The precipitate of calcium oxalate may be converted into calcium oxide

by ignition without previous drying. After burning the filter, it may

be ignited for three quarters of an hour in a platinum crucible at

the highest heat of the Bunsen or Tirrill burner, and finally for ten

minutes at the blast lamp (Note 6). Repeat the heating over the blast

lamp until the weight is constant. As the calcium oxide absorbs

moisture from the air, it must (after cooling) be weighed as rapidly

as possible.

The precipitate may, if preferred, be placed in a weighted porcelain

crucible. After burning off the filter and heating for ten minutes the

calcium precipitate may be converted into calcium sulphate by placing

2 cc. of dilute sulphuric acid in the crucible (cold), heating the

covered crucible very cautiously over a low flame to drive off the

excess of acid, and finally at redness to constant weight (Note 7).

From the weight of the oxide or sulphate, calculate the percentage of

the calcium (Ca) in the limestone, remembering that only one fifth of

the total solution is used for this determination.

[Note 1: 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 in a

graduated flask or by means of a pipette.]

[Note 2: 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.]

[Note 3: 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.]

[Note 4: 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 113 also

apply here. The reaction is

C\_{2}O\_{4}^{--} + Ca^{++} --> [CaC\_{2}O\_{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\_{2}O\_{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\_{2}O\_{4}^{--} ions in solution, more of the oxalate passes into

solution to re-establish equilibrium, and this process repeats itself

until all is dissolved.

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\_{2}O\_{4}^{--} ions in the solution to recombine to

form [CaC\_{2}O\_{4}], which is precipitated in the absence of the

H^{+} ions. It is well at this point to add a small excess of

C\_{2}O\_{4}^{--} ions in the form of ammonium oxalate to decrease the

solubility of the precipitate.

The oxalate precipitate consists mainly of CaC\_{2}O\_{4}.H\_{2}O when

thrown down.]

[Note 5: 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.]

[Note 6: On ignition the calcium oxalate loses carbon dioxide and

carbon monoxide, leaving calcium oxide:

CaC\_{2}O\_{4}.H\_{2}O --> CaO + CO\_{2} + CO + H\_{2}O.

For small weights of the oxalate (0.6 gram or less) this reaction may

be brought about in a platinum crucible 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.]

[Note 7: The heat required to burn the filter, and that subsequently

applied as described, will convert most of the calcium oxalate to

calcium carbonate, which is changed to sulphate by the sulphuric acid.

The reactions involved are

CaC\_{2}O\_{4} --> CaCO\_{3} + CO,

CaCO\_{3} + H\_{2}SO\_{4} --> CaSO\_{4} + H\_{2}O + CO\_{2}.

If a porcelain crucible is employed for ignition, this conversion to

sulphate is to be preferred, as a complete conversion to oxide is

difficult to accomplish.]

[Note 8: The determination of the calcium may be completed

volumetrically by washing the calcium oxalate precipitate from

the filter into dilute sulphuric acid, warming, and titrating

the liberated oxalic acid with a standard solution of potassium

permanganate as described on page 72. When a considerable number of

analyses are to be made, this procedure will save much of the time

otherwise required for ignition and weighing.]

DETERMINATION OF MAGNESIUM

PROCEDURE.--Evaporate the acidified filtrates from the calcium

precipitates until the salts begin to crystallize, but do !not!

evaporate to dryness (Note 1). 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 a precipitate

has appeared. Heat the clear solution to boiling; remove the burner

and add 25 cc. of a solution of disodium phosphate. Then add slowly

dilute ammonia (1 volume strong ammonia (sp. gr. 0.90) and 9 volumes

water) as long as a precipitate continues to form. Finally, add a

volume of concentrated ammonia (sp. gr. 0.90) equal to one third of

the volume of the solution, and allow the whole to stand for 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 122, including; the reprecipitation (Note 2),

except that 3 cc. of disodium phosphate solution are added before the

reprecipitation of the magnesium ammonium phosphate instead of

the magnesia mixture there prescribed. From the weight of the

pyrophosphate, calculate the percentage of magnesium oxide (MgO) in

the sample of limestone. Remember that the pyrophosphate finally

obtained is from one fifth of the original sample.

[Note 1: 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.]

[Note 2: 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 best be 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 disodium 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

!Absorption Apparatus!

[Illustration: Fig. 3]

The apparatus required for the determination of the carbon dioxide

should be arranged as shown in the cut (Fig. 3). The flask (A) is

an ordinary wash bottle, which should be nearly filled with dilute

hydrochloric acid (100 cc. acid (sp. gr. 1.12) and 200 cc. of water).

The flask is connected by rubber tubing (a) with the glass tube (b)

leading nearly to the bottom of the evolution flask (B) and having its

lower end bent upward and drawn out to small bore, so that the carbon

dioxide evolved from the limestone cannot bubble back into (b). The

evolution flask should preferably be a wide-mouthed Soxhlet extraction

flask of about 150 cc. capacity because of the ease with which tubes

and stoppers may be fitted into the neck of a flask of this type. The

flask should be fitted with a two-hole rubber stopper. The condenser

(C) may consist of a tube with two or three large bulbs blown in

it, for use as an air-cooled condenser, or it may be a small

water-jacketed condenser. The latter is to be preferred if a number of

determinations are to be made in succession.

A glass delivery tube (c) leads from the condenser to the small U-tube

(D) containing some glass beads or small pieces of glass rod and 3 cc.

of a saturated solution of silver sulphate, with 3 cc. of concentrated

sulphuric acid (sp. gr. 1.84). The short rubber tubing (d) connects

the first U-tube to a second U-tube (E) which is filled with small

dust-free lumps of dry calcium chloride, with 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 cut off level with, or preferably

forced a little below, the top of the U-tube, and then neatly sealed

with sealing wax.

The carbon dioxide may be absorbed in a tube containing soda lime

(F) or in a Geissler bulb (F') containing a concentrated solution

of potassium hydroxide (Note 2). The tube (F) is a glass-stoppered

side-arm U-tube in which the side toward the evolution flask and one

half of the other side are filled with small, dust-free lumps of soda

lime of good quality (Note 3). Since soda lime contains considerable

moisture, the other half of the right side of the tube is filled with

small lumps of dry, dust-free calcium chloride to retain the moisture

from the soda lime. Loose plugs of cotton are placed at the top of

each arm and between the soda lime and the calcium chloride.

The Geissler bulb (F'), if used, should be filled with potassium

hydroxide solution (1 part of solid potassium hydroxide dissolved in

two parts of water) until each small bulb is about two thirds full

(Note 4). A small tube containing calcium chloride is connected with

the Geissler bulb proper by a ground joint and should be wired to the

bulb for safety. This is designed to retain any moisture from the

hydroxide solution. A piece of clean, fine copper wire is so attached

to the bulb that it can be hung from the hook above a balance pan, or

other support.

The small bottle (G) with concentrated sulphuric acid (sp. gr. 1.84)

is so arranged that the tube (f) barely dips below the surface. This

will prevent the absorption of water vapor by (F) or (F') and serves

as an aid in regulating the flow of air through the apparatus. (H) is

an aspirator bottle of about four liters capacity, filled with water;

(k) is a safety tube and a means of refilling (H); (h) is a screw

clamp, and (K) a U-tube filled with soda lime.

[Note 1: The air current, which is subsequently drawn through the

apparatus, to sweep all of the carbon dioxide into the absorption

apparatus, is likely to carry with it some hydrochloric acid from

the evolution flask. This acid is retained by the silver sulphate

solution. The addition of concentrated sulphuric acid to this solution

reduces its vapor pressure so far that very little water is carried on

by the air current, and this slight amount is absorbed by the calcium

chloride in (E). As the calcium chloride frequently contains a small

amount of a basic material which would absorb carbon dioxide, it is

necessary to pass carbon dioxide through (E) for a short time and then

drive all the gas out with a dry air current for thirty minutes before

use.]

[Note 2: Soda-lime absorption tubes are to be preferred if a

satisfactory quality of soda lime is available and the number of

determinations to be made successively is small. The potash bulbs will

usually permit of a larger number of successive determinations without

refilling, but they require greater care in handling and in the

analytical procedure.]

[Note 3: Soda lime is a mixture of sodium and calcium hydroxides. Both

combine with carbon dioxide to form carbonates, with the evolution

of water. Considerable heat is generated by the reaction, and the

temperature of the tube during absorption serves as a rough index of

the progress of the reaction through the mass of soda lime.

It is essential that soda lime of good quality for analytical purposes

should be used. The tube should not contain dust, as this is likely to

be swept away.]

[Note 4: The solution of the hydroxide for use in the Geissler bulb

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.

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 Analysis!

PROCEDURE.-- Weigh out into the flask (B) about 1 gram of limestone.

Cover it with 15 cc. of water. Weigh the absorption apparatus (F)

or (F') accurately after allowing it to stand for 30 minutes in the

balance case, and wiping it carefully with a lintless cloth, taking

care to handle it as little as possible after wiping (Note 1). Connect

the absorption apparatus with (e) and (f). If a soda-lime tube is

used, be sure that the arm containing the soda lime is next the tube

(E) and that the glass stopcocks are open.

To be sure that the whole apparatus is airtight, disconnect the rubber

tube from the flask (A), making sure that the tubes (a) and (b) do not

contain any hydrochloric acid, close the pinchcocks (a) and (k) and

open (h). No bubbles should pass through (D) or (G) after a few

seconds. When assured that the fittings are tight, close (h) and open

(a) cautiously to admit air to restore atmospheric pressure. This

precaution is essential, as a sudden inrush of air will project liquid

from (D) or (F'). Reconnect the rubber tube with the flask (A).

Open the pinchcocks (a) and (k) and blow over about 10 cc. of the

hydrochloric acid from (A) into (B). When the action of the acid

slackens, blow over (slowly) another 10 cc.

The rate of gas evolution should not exceed for more than a few

seconds that at which about two bubbles per second pass through (G)

(Note 2). Repeat the addition of acid in small portions until the

action upon the limestone seems to be at an end, taking care to close

(a) after each addition of acid (Note 3). Disconnect (A) and connect

the rubber tubing with the soda-lime tube (K) and open (a). Then close

(k) and open (h), regulating the flow of water from (H) in such a way

that about two bubbles per second pass through (G). Place a small

flame under (B) and !slowly! raise the contents to boiling and boil

for three minutes. Then remove the burner from under (B) and continue

to draw air through the apparatus for 20-30 minutes, or until (H)

is emptied (Note 4). Remove the absorption apparatus, closing the

stopcocks on (F) or stoppering the open ends of (F'), leave the

apparatus in the balance case for at least thirty minutes, wipe it

carefully and weigh, after opening the stopcocks (or removing plugs).

The increase in weight is due to absorption of CO\_{2}, from which its

percentage in the sample may be calculated.

After cleaning (B) and refilling (H), the apparatus is ready for the

duplicate analysis.

[Note 1: The absorption tubes or bulbs have large surfaces on which

moisture may collect. By allowing them to remain in the balance case

for some time before weighing, the amount of moisture absorbed on the

surface is as nearly constant as practicable during two weighings, and

a uniform temperature is also assured. The stopcocks of the U-tube

should be opened, or the plugs used to close the openings of the

Geissler bulb should be removed before weighing in order that the air

contents shall always be at atmospheric pressure.]

[Note 2: If the gas passes too rapidly into the absorption apparatus,

some carbon dioxide may be carried through, not being completely

retained by the absorbents.]

[Note 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 H^{+} ions

of the mineral acid, the CO\_{3}^{--} ions form [H\_{2}CO\_{3}]. This

is not only a weak acid which, by its formation, diminishes the

concentration of the CO\_{3}^{--} ions, thus causing more of the

carbonate to dissolve to re-establish equilibrium, but it is also an

unstable compound and breaks down into carbon dioxide and water.]

[Note 4: 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

(K) containing soda lime, which removes any carbon dioxide which may

be in it.]

DETERMINATION OF LEAD, COPPER, IRON, AND ZINC IN BRASS

ELECTROLYTIC SEPARATIONS

!General Discussion!

When a direct current of electricity passes from one electrode to

another through solutions of electrolytes, the individual ions present

in these solutions tend to move toward the electrode of opposite

electrical charge to that which each ion bears, and to be discharged

by that electrode. Whether or not such discharge actually occurs in

the case of any particular ion depends upon the potential (voltage) of

the current which is passing through the solution, since for each ion

there is, under definite conditions, a minimum potential below which

the discharge of the ion cannot be effected. By taking advantage

of differences in discharge-potentials, it is possible to effect

separations of a number of the metallic ions by electrolysis, and at

the same time to deposit the metals in forms which admit of direct

weighing. In this way the slower procedures of precipitation and

filtration may frequently be avoided. The following paragraphs present

a brief statement of the fundamental principles and conditions

underlying electro-analysis.

The total energy of an electric current as it passes through a

solution is distributed among three factors, first, its potential,

which is measured in volts, and corresponds to what is called "head"

in a stream of water; second, current strength, which is measured

in amperes, and corresponds to the volume of water passing a

cross-section of a stream in a given time interval; and third, the

resistance of the conducting medium, which is measured in ohms. The

relation between these three factors is expressed by Ohm's law,

namely, that !I = E/R!, when I is current strength, E potential, and R

resistance. It is plain that, for a constant resistance, the

strength of the current and its potential are mutually and directly

interdependent.

As already stated, the applied electrical potential determines whether

or not deposition of a metal upon an electrode actually occurs. The

current strength determines the rate of deposition and the physical

characteristics of the deposit. The resistance of the solution is

generally so small as to fall out of practical consideration.

Approximate deposition-potentials have been determined for a number

of the metallic elements, and also for hydrogen and some of the

acid-forming radicals. The values given below are those required

for deposition from normal solutions at ordinary temperatures

with reference to a hydrogen electrode. They must be regarded as

approximate, since several disturbing factors and some secondary

reactions render difficult their exact application under the

conditions of analysis. They are:

Zn Cd Fe Ni Pb H Cu Sb Hg Ag SO\_{4}

+0.77 +0.42 +0.34 +0.33 +0.13 0 -0.34 -0.67 -0.76 -0.79 +1.90

From these data it is evident that in order to deposit copper from a

normal solution of copper sulphate a minimum potential equal to the

algebraic sum of the deposition-potentials of copper ions and sulphate

ions must be applied, that is, +1.56 volts. The deposition of zinc

from a solution of zinc sulphate would require +2.67 volts, but, since

the deposition of hydrogen from sulphuric acid solution requires only

+1.90 volts, the quantitative deposition of zinc by electrolysis from

a sulphuric acid solution of a zinc salt is not practicable. On the

other hand, silver, if present in a solution of copper sulphate, would

deposit with the copper.

The foregoing examples suffice to illustrate the application of the

principle of deposition potentials, but it must further be noted

that the values stated apply to normal solutions of the compounds in

question, that is, to solutions of considerable concentrations. As the

concentration of the ions diminishes, and hence fewer ions approach

the electrodes, somewhat higher voltages are required to attract and

discharge them. From this it follows that the concentrations should be

kept as high as possible to effect complete deposition in the least

practicable time, or else the potentials applied must be progressively

increased as deposition proceeds. In practice, the desired result is

obtained by starting with small volumes of solution, using as large an

electrode surface as possible, and by stirring the solution to bring

the ions in contact with the electrodes. This is, in general, a more

convenient procedure than that of increasing the potential of the

current during electrolysis, although that method is also used.

As already stated, those ions in a solution of electrolytes will first

be discharged which have the lowest deposition potentials, and so

long as these ions are present around the electrode in considerable

concentration they, almost alone, are discharged, but, as their

concentration diminishes, other ions whose deposition potentials are

higher but still within that of the current applied, will also begin

to separate. For example, from a nitric acid solution of copper

nitrate, the copper ions will first be discharged at the cathode, but

as they diminish in concentration hydrogen ions from the acid (or

water) will be also discharged. Since the hydrogen thus liberated is a

reducing agent, the nitric acid in the solution is slowly reduced to

ammonia, and it may happen that if the current is passed through for a

long time, such a solution will become alkaline. Oxygen is liberated

at the anode, but, since there is no oxidizable substance present

around that electrode, it escapes as oxygen gas. It should be noted

that, in general, the changes occurring at the cathode are reductions,

while those at the anode are oxidations.

For analytical purposes, solutions of nitrates or sulphates of the

metals are preferable to those of the chlorides, since liberated

chlorine attacks the electrodes. In some cases, as for example, that

of silver, solution of salts forming complex ions, like that of

the double cyanide of silver and potassium, yield better metallic

deposits.

Most metals are deposited as such upon the cathode; a few, notably

lead and manganese, separate in the form of dioxides upon the anode.

It is evidently important that the deposited material should be so

firmly adherent that it can be washed, dried, and weighed without

loss in handling. To secure these conditions it is essential that the

current density (that is, the amount of current per unit of area of

the electrodes) shall not be too high. In prescribing analytical

conditions it is customary to state the current strength in "normal

densities" expressed in amperes per 100 sq. cm. of electrode surface,

as, for example, "N.D\_{100} = 2 amps."

If deposition occurs too rapidly, the deposit is likely to be spongy

or loosely adherent and falls off on subsequent treatment. This places

a practical limit to the current density to be employed, for a given

electrode surface. The cause of the unsatisfactory character of

the deposit is apparently sometimes to be found in the coincident

liberation of considerable hydrogen and sometimes in the failure of

the rapidly deposited material to form a continuous adherent surface.

The effect of rotating electrodes upon the character of the deposit is

referred to below.

The negative ions of an electrolyte are attracted to the anode and are

discharged on contact with it. Anions such as the chloride ion yield

chlorine atoms, from which gaseous chlorine molecules are formed

and escape. The radicals which compose such ions as NO\_{3}^{-} or

SO\_{4}^{--} are not capable of independent existence after discharge,

and break down into oxygen and N\_{2}O\_{5} and SO\_{3} respectively. The

oxygen escapes and the anhydrides, reacting with water, re-form nitric

and sulphuric acids.

The law of Faraday expresses the relation between current strength and

the quantities of the decomposition products which, under constant

conditions, appear at the electrodes, namely, that a given quantity

of electricity, acting for a given time, causes the separation of

chemically equivalent quantities of the various elements or radicals.

For example, since 107.94 grams of silver is equivalent to 1.008 grams

of hydrogen, and that in turn to 8 grams of oxygen, or 31.78 grams of

copper, the quantity of electricity which will cause the deposit of

107.94 grams of silver in a given time will also separate the weights

just indicated of the other substances. Experiments show that a

current of one ampere passing for one second, i.e., a coulomb of

electricity, causes the deposition of 0.001118 gram of silver from a

normal solution of a silver salt. The number of coulombs required to

deposit 107.94 grams is 107.94/0.001118 or 96,550 and the same number

of coulombs will also cause the separation of 1.008 grams of hydrogen,

8 grams of oxygen or 31.78 grams of copper. While it might at first

appear that Faraday's law could thus be used as a basis for the

calculation of the time required for the deposition of a given

quantity of an electrolyte from solution, it must be remembered that

the law expresses what occurs when the concentration of the ions in

the solution is kept constant, as, for example, when the anode in

a silver salt solution is a plate of metallic silver. Under the

conditions of electro-analysis the concentration of the ions is

constantly diminishing as deposition proceeds and the time actually

required for complete deposition of a given weight of material by

a current of constant strength is, therefore, greater than that

calculated on the basis of the law as stated above.

The electrodes employed in electro-analysis are almost exclusively

of platinum, since that metal alone satisfactorily resists chemical

action of the electrolytes, and can be dried and weighed without

change in composition. The platinum electrodes may be used in the

form of dishes, foil or gauze. The last, on account of the ease of

circulation of the electrolyte, its relatively large surface in

proportion to its weight and the readiness with which it can be washed

and dried, is generally preferred.

Many devices have been described by the use of which the electrode

upon which deposition occurs can be mechanically rotated. This has an

effect parallel to that of greatly increasing the electrode surface

and also provides a most efficient means of stirring the solution.

With such an apparatus the amperage may be increased to 5 or even 10

amperes and depositions completed with great rapidity and accuracy. It

is desirable, whenever practicable, to provide a rotating or stirring

device, since, for example, the time consumed in the deposition of the

amount of copper usually found in analysis may be reduced from the

20 to 24 hours required with stationary electrodes, and unstirred

solutions, to about one half hour.

DETERMINATION OF COPPER AND LEAD

PROCEDURE.--Weigh out two portions of about 0.5 gram each (Note 1)

into tall, slender lipless beakers of about 100 cc. capacity. Dissolve

the metal in a solution of 5 cc. of dilute nitric acid (sp. gr. 1.20)

and 5 cc. of water, heating gently, and keeping the beaker covered.

When the sample has all dissolved (Note 2), wash down the sides of the

beaker and the bottom of the watch-glass with water and dilute the

solution to about 50 cc. Carefully heat to boiling and boil for a

minute or two to expel nitrous fumes.

Meanwhile, four platinum electrodes, two anodes and two cathodes,

should be cleaned by dipping in dilute nitric acid, washing with water

and finally with 95 per cent alcohol (Note 3). The alcohol may be

ignited and burned off. The electrodes are then cooled in a desiccator

and weighed. Connect the electrodes 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. The beaker containing the solution

should then be raised into place from below the electrodes until the

latter reach nearly to the bottom of the beaker. The support for the

beaker must be so arranged that it can be easily raised or lowered.

If the electrolytic apparatus is provided with a mechanism for the

rotation of the electrode or stirring of the electrolyte, proceed as

follows: Arrange the resistance in the circuit to provide a direct

current of about one ampere. Pass this current through the solution

to be electrolyzed, and start the rotating mechanism. Keep the beaker

covered as completely as possible, using a split watch-glass (or other

device) to avoid loss by spattering. When the solution is colorless,

which is usually the case after about 35 minutes, rinse off the cover

glass, wash down the sides of the beaker, add about 0.30 gram of urea

and continue the electrolysis for another five minutes (Notes 4 and

5).

If stationary electrodes are employed, the current strength should be

about 0.1 ampere, which may, after 12 to 15 hours, be increased to 0.2

ampere. The time required for complete deposition is usually from 20

to 24 hours. It is advisable to add 5 cc. of nitric acid (sp. gr. 1.2)

if the electrolysis extends over this length of time. No urea is added

in this case.

When the deposition of the copper appears to be complete, stop the

rotating mechanism and slowly lower the beaker with the left hand,

directing at the same time a stream of water from a wash bottle on

both electrodes. Remove the beaker, shut off the current, and, if

necessary, complete the washing of the electrodes (Note 6). Rinse the

electrodes cautiously with alcohol and heat them in a hot closet until

the alcohol has just evaporated, but no longer, since the copper is

likely to oxidize at the higher temperature. (The alcohol may be

removed by ignition if care is taken to keep the electrodes in motion

in the air so that the copper deposit is not too strongly heated at

any one point.)

Test the solution in the beaker for copper as follows, remembering

that it is to be used for subsequent determinations of iron and zinc:

Remove about 5 cc. and add a slight excess of ammonia. Compare the

mixture with some distilled water, holding both above a white surface.

The solution should not show any tinge of blue. If the presence of

copper is indicated, add the test portion to the main solution,

evaporate the whole to a volume of about 100 cc., and again

electrolyze with clean electrodes (Note 7).

After cooling the electrodes in a desiccator, weigh them and from the

weight of copper on the cathode and of lead dioxide (PbO\_{2}) on the

anode, calculate the percentage of copper (Cu) and of lead (Pb) in the

brass.

[Note 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.]

[Note 2: If a white residue remains upon treatment of the alloy with

nitric acid, it indicates the presence of tin. The material is not,

therefore, a true brass. This may be treated as follows: Evaporate the

solution to dryness, moisten the residue with 5 cc. of dilute nitric

acid (sp. gr. 1.2) and add 50 cc. of hot water. Filter off the

meta-stannic acid, wash, ignite in porcelain and weigh as SnO\_{2}.

This oxide is never wholly free from copper and must be purified for

an exact determination. If it does not exceed 2 per cent of the alloy,

the quantity of copper which it contains may usually be neglected.]

[Note 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 cleaning.]

[Note 4: Of the ions in solution, the H^{+}, Cu^{++}, Zn^{++}, and

Fe^{+++} ions tend to move toward the cathode. The NO\_{3}^{-} ions and

the lead, probably in the form of PbO\_{2}^{--} ions, move toward the

anode. At the cathode the Cu^{++} ions are discharged and plate out as

metallic copper. This alone occurs while the solution is relatively

concentrated. Later on, H^{+} ions are also discharged. In the

presence of considerable quantities of H^{+} ions, as in this acid

solution, no Zn^{++} or Fe^{+++} ions are discharged because of their

greater deposition potentials. At the anode the lead is deposited as

PbO\_{2} and oxygen is evolved.

For the reasons stated on page 141 care must be taken that the

solution does not become alkaline if the electrolysis is long

continued.]

[Note 5: Urea reacts with nitrous acid, which may be formed in the

solution as a result of the reducing action of the liberated hydrogen.

Its removal promotes the complete precipitation of the copper. The

reaction is

CO(NH\_{2})\_{2} + 2HNO\_{2} --> CO\_{2} + 2N\_{2} + 3H\_{2}O.]

[Note 6: The electrodes must be washed nearly or quite free from

the nitric acid solution before the circuit is broken to prevent

re-solution of the copper.

If several solutions are connected in the same circuit it is obvious

that some device must be used to close the circuit as soon as the

beaker is removed.]

[Note 7: The electrodes upon which the copper has been deposited

may be cleaned by immersion in warm nitric acid. To remove the lead

dioxide, add a few crystals of oxalic acid to the nitric acid.]

DETERMINATION OF IRON

Most brasses contain small percentages of iron (usually not over 0.1

per cent) which, unless removed, is precipitated as phosphate and

weighed with the zinc.

PROCEDURE.--To the solution from the precipitation of copper and

lead by electrolysis, add dilute ammonia (sp. gr. 0.96) until the

precipitate of zinc hydroxide which first forms re-dissolves, leaving

only a slight red precipitate of ferric hydroxide. Filter off the

iron precipitate, using a washed filter, and wash five times with hot

water. Test a portion of the last washing with a dilute solution of

ammonium sulphide to assure complete removal of the zinc.

The precipitate may then be ignited and weighed as ferric oxide, as

described on page 110.

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

DETERMINATION OF ZINC

PROCEDURE.--Acidify the filtrate from the iron determination with

dilute nitric acid. Concentrate it to 150 cc. Add to the cold solution

dilute ammonia (sp. gr. 0.96) cautiously until it barely smells of

ammonia; then add !one drop! of a dilute solution of litmus (Note 1),

and drop in, with the aid of a dropper, dilute nitric acid 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. (For this

calculation the approximate percentage of zinc is that found by

subtracting the sum of the percentages of the copper, lead and iron

from 100 per cent.) Keep the solution just below boiling for fifteen

minutes, stirring frequently (Note 2). If at the end of this time the

amorphous precipitate has become crystalline, allow the solution to

cool for about four hours, although a longer time does no harm (Note

3), and filter upon an asbestos filter in a porcelain Gooch crucible.

The filter is prepared as described on page 103, and should be dried

to constant weight at 105°C.

[Footnote 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.]

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 (Note 4). Dry the crucible and precipitate for an hour at

105°C., and finally to constant weight (Note 5). The filtrate should

be made alkaline with ammonia and tested for zinc with a few drops of

ammonium sulphide, allowing it to stand (Notes 6, 7 and 8).

From the weight of the zinc ammonium phosphate (ZnNH\_{4}PO\_{4})

calculate the percentage of the zinc (Zn) in the brass.

[Note 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.]

[Note 2: The precipitate which first forms is amorphous, and may have

a variable composition. On standing it becomes crystalline and then

has the composition ZnNH\_{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.]

[Note 3: In a carefully neutralized solution containing a considerable

excess of the precipitant, and also ammonium salts, the separation

of the zinc is complete after standing four hours. 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}^{++}.]

[Note 4: 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.]

[Note 5: The precipitate may be ignited and weighed as

Zn\_{2}P\_{2}O\_{7}, 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.]

[Note 6: If the ammonium sulphide produced 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, filtered off, dried, and weighed, and the weight added to

that of the main precipitate.]

[Note 7: 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.]

[Note 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 silicates, or artificial silicates such as slags and

some of the cements, a comparatively few can be completely decomposed

by treatment with acids, but by far the larger number require fusion

with an alkaline flux to effect decomposition and solution

for analysis. The procedure given below applies to silicates

undecomposable by acids, of which the mineral feldspar is taken as a

typical example. Modifications of the procedure, which are applicable

to silicates which are completely or partially decomposable by acids,

are given in the Notes on page 155.

PREPARATION OF THE SAMPLE

Grind about 3 grams of the mineral in an agate mortar (Note 1) until

no grittiness is to be detected, 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, and the

process of sifting and grinding repeated until the entire sample

passes through the sieve.

[Note 1: If the sample of feldspar for analysis is in the massive or

crystalline form, it should be crushed in an iron mortar until the

pieces are about half the size of a pea, and then transferred to a

steel mortar, in which they are reduced to a coarse powder. 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 final grinding in an agate mortar 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 not more than the

quantity of the feldspar needed for analysis. The mineral must be

thoroughly mixed after the grinding.]

FUSION AND SOLUTION

PROCEDURE.--Weigh into platinum crucibles two portions of the ground

feldspar of about 0.8 gram each. Weigh on rough balances two portions

of anhydrous sodium carbonate, each amounting to about six times the

weight of the feldspar taken for analysis (Note 1). 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 end of which has been recently heated and rounded in a flame

and slowly cooled. 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 (Note 2).

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 116. Disintegrate the mass by placing it in a previously prepared

mixture of 100 cc. of water and 50 cc. of dilute hydrochloric acid

(sp. gr. 1.12) in a covered casserole (Note 3). Clean the crucible and

lid by means of a little hydrochloric acid, adding this acid to the

main solution (Notes 4 and 5).

[Note 1: 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.]

[Note 2: During the fusion the feldspar, which, when pure, is 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 combines 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 into basic carbonate, or the oxide. The calcium and

magnesium, if present, are changed to carbonates or oxides.

The heat is applied gently to prevent a too violent reaction when

fusion first takes place.]

[Note 3: The solution of a silicate by a strong acid is the result of

the combination of the H^{+} ions of the acid and the silicate ions

of the silicate to form a 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 re-establish

the disturbed equilibrium. This process repeats itself until all of

the silicate is brought into solution.

Whether the resulting solution of the silicate contains ortho-silicic

acid (H\_{4}SiO\_{4}) or whether it is a colloidal solution of some

other less hydrated acid, such as meta-silicic acid (H\_{2}SiO\_{3}),

is a matter that is still debatable. It is certain, however, that the

gelatinous material which readily separates from such solutions is of

the nature of a hydrogel, that is, a colloid which is insoluble in

water. This substance when heated to 100°C., or higher, is completely

dehydrated, leaving only the anhydride, SiO\_{2}. The changes may be

represented by the equation:

SiO\_{3}^{--} + 2H^{+} --> [H\_{2}SiO\_{3}] --> H\_{2}O + SiO\_{2}.]

[Note 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.]

[Note 5: A gritty residue remaining after the disintegration of

the fused mass by acid 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.]

DEHYDRATION AND FILTRATION

PROCEDURE.--Evaporate the solution of the fusion to dryness, stirring

frequently until the residue is a dry powder. Moisten the residue with

5 cc. of strong hydrochloric acid (sp. gr. 1.20) and evaporate again

to dryness. Heat the residue for at least one hour at a temperature

of 110°C. (Note 1). Again moisten the residue with concentrated

hydrochloric acid, warm gently, making sure that the acid comes into

contact with the whole of the residue, dilute to about 200 cc. and

bring to boiling. Filter off the silica without much delay (Note 2),

and wash five times with warm dilute hydrochloric acid (one part

dilute 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 wash with water until free from chlorides, discarding these

washings. Evaporate the original filtrate to dryness, dehydrate at

110°C. for one hour (Note 3), and proceed as before, using a second

filter to collect the silica after the second dehydration. Wash this

filter with warm, dilute hydrochloric acid (Note 4), and finally with

hot water until free from chlorides.

[Note 1: 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.

Immediate treatment of the fused mass with strong acid is likely

to cause a semi-gelatinous silicic acid to separate at once and to

inclose alkali salts or alumina.

A flocculent residue will often remain after the decomposition of the

fused mass is effected. This is usually partially dehydrated silicic

acid and does not require further treatment at this point. 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.]

[Note 2: To obtain an approximately 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 residual salts in the particles of silica. The

filtration should take place without delay, as the dehydrated silica

slowly dissolves in hydrochloric acid on standing.]

[Note 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.

It is probable that temperatures above 100°C. are 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 the admirable monograph on "The Analysis of Silicate and

Carbonate Rocks," Bulletin No. 700 of the United States Geological

Survey.

The double evaporation and filtration spoken of above are essential

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 for silica the precipitate produced in the filtrate by

ammonium hydroxide by fusing it with acid potassium sulphate and

solution of the fused mass in water. The insoluble silica is filtered,

washed, and weighed, and the weight added to the weight of silica

previously obtained.]

[Note 4: 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.]

IGNITION AND TESTING OF SILICA

PROCEDURE.--Transfer the two washed filters belonging to each

determination to a platinum crucible, which need not be previously

weighed, and burn off the filter (Note 1). Ignite for thirty minutes

over the blast lamp with the cover on the crucible, 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 not to

come into contact with the acid or to inhale its fumes (Note 2!).

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 crucible and residue.

Deduct this weight from the previous weight of crucible and impure

silica, and from the difference calculate the percentage of silica in

the sample (Note 3).

[Note 1: 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.]

[Note 2: Notwithstanding all precautions, the ignited precipitate of

silica is rarely wholly pure. It is tested by volatilisation 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.]

[Note 3: 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.]

[Note 4: If the silicate to be analyzed is shown by a previous

qualitative examination to be completely decomposable, it may be

directly treated with hydrochloric acid, the solution evaporated to

dryness, and the silica dehydrated and further treated as described in

the case of the feldspar after fusion.

A silicate which gelatinizes on treatment with acids should be mixed

first with a little water, and the strong acid added in small portions

with stirring, otherwise the gelatinous silicic acid incloses

particles of the original silicate and prevents decomposition. The

water, by separating the particles and slightly lessening the rapidity

of action, prevents this difficulty. This procedure is one which

applies in general to the solution of fine mineral powders in acids.

If a small residue remains undecomposed by the treatment of the

silicate with acid, this may be filtered, washed, ignited and fused

with sodium carbonate and a solution of the fused mass added to the

original acid solution. This double procedure has an advantage, in

that it avoids adding so large a quantity of sodium salts as is

required for disintegration of the whole of the silicate by the fusion

method.]

PART IV

STOICHIOMETRY

The problems with which the analytical chemist has to deal are not, as

a matter of actual fact, difficult either to solve or to understand.

That they appear difficult to many students is due to the fact that,

instead of understanding the principles which underlie each of the

small number of types into which these problems may be grouped, each

problem is approached as an individual puzzle, unrelated to others

already solved or explained. This attitude of mind should be carefully

avoided.

It is obvious that ability to make the calculations necessary for

the interpretation of analytical data is no less important than the

manipulative skill required to obtain them, and that a moderate time

spent in the careful study of the solutions of the typical problems

which follow may save much later embarrassment.

1. It is often necessary to calculate what is known as a "chemical

factor," or its equivalent logarithmic value called a "log factor,"

for the conversion of the weight of a given chemical substance into an

equivalent weight of another substance. This is, in reality, a very

simple problem in proportion, making use of the atomic or molecular

weights of the substances in question which are chemically equivalent

to each other. One of the simplest cases of this sort is the

following: What is the factor for the conversion of a given weight of

barium sulphate (BaSO\_{4}) into an equivalent weight of sulphur (S)?

The molecular weight of BaSO\_{4} is 233.5. There is one atom of S in

the molecule and the atomic weight of S is 32.1. The chemical factor

is, therefore, 32.1/233.5, or 0.1375 and the weight of S corresponding

to a given weight of BaSO\_{4} is found by multiplying the weight of

BaSO\_{4} by this factor. If the problem takes the form, "What is

the factor for the conversion of a given weight of ferric oxide

(Fe\_{2}O\_{3}) into ferrous oxide (FeO), or of a given weight of

mangano-manganic oxide (Mn\_{3}O\_{4}) into manganese (Mn)?" the

principle involved is the same, but it must then be noted that, in the

first instance, each molecule of Fe\_{2}O\_{3} will be equivalent to two

molecules of FeO, and in the second instance that each molecule of

Mn\_{3}O\_{4} is equivalent to three atoms of Mn. The respective factors

then become

(2FeO/Fe\_{2}O\_{3}) or (143.6/159.6) and (3Mn/Mn\_{3}O\_{4}) or

(164.7/228.7).

It is obvious that the arithmetical processes involved in this type

of problem are extremely simple. It is only necessary to observe

carefully the chemical equivalents. It is plainly incorrect to express

the ratio of ferrous to ferric oxide as (FeO/Fe\_{2}O\_{3}), since each

molecule of the ferric oxide will yield two molecules of the ferrous

oxide. Mistakes of this sort are easily made and constitute one of the

most frequent sources of error.

2. A type of problem which is slightly more complicated in appearance,

but exactly comparable in principle, is the following: "What is the

factor for the conversion of a given weight of ferrous sulphate

(FeSO\_{4}), used as a reducing agent against potassium permanganate,

into the equivalent weight of sodium oxalate (Na\_{2}C\_{2}O\_{4})?" To

determine the chemical equivalents in such an instance it is necessary

to inspect the chemical reactions involved. These are:

10FeSO\_{4} + 2KMnO\_{4} + 8H\_{2}SO\_{4} --> 5Fe\_{2}(SO\_{4})\_{3} +

K\_{2}SO\_{4} + 2MnSO\_{4} + 8H\_{2}O,

5Na\_{2}C\_{2}O\_{4} + 2KMnO\_{4} + 8H\_{2}SO\_{4} --> 5Na\_{2}SO\_{4} +

10CO\_{2} + K\_{2}SO\_{4} + 2MnSO\_{4} + 8H\_{2}O.

It is evident that 10FeSO\_{4} in the one case, and 5Na\_{2}C\_{2}O\_{4}

in the other, each react with 2KMnO\_{4}. These molecular

quantities are therefore equivalent, and the factor becomes

(10FeSO\_{4}/5Na\_{2}C\_{2}O\_{4}) or (2FeSO\_{4}/Na\_{2}C\_{2}O\_{4}) or

(303.8/134).

Again, let it be assumed that it is desired to determine the

factor required for the conversion of a given weight of potassium

permanganate (KMnO\_{4}) into an equivalent weight of potassium

bichromate (K\_{2}Cr\_{2}O\_{7}), each acting as an oxidizing agent

against ferrous sulphate. The reactions involved are:

10FeSO\_{4} + 2KMnO\_{4} + 8H\_{2}SO\_{4} --> 5Fe\_{2}(SO\_{4})\_{3} +

K\_{2}SO\_{4} + 2MnSO\_{4} + 8H\_{2}O,

6FeSO\_{4} + K\_{2}Cr\_{2}O\_{7} + 7H\_{2}SO\_{4} --> 3Fe\_{2}(SO\_{3})\_{3} +

K\_{2}SO\_{4} + Cr\_{2}(SO\_{4})\_{3} + 7H\_{2}O.

An inspection of these equations shows that 2KMO\_{4} react with

10FeSO\_{4}, while K\_{2}Cr\_{2}O\_{7} reacts with 6FeSO\_{4}. These are

not equivalent, but if the first equation is multiplied by 3 and the

second by 5 the number of molecules of FeSO\_{4} is then the same in

both, and the number of molecules of KMnO\_{4} and K\_{2}Cr\_{2}O\_{7}

reacting with these 30 molecules become 6 and 5 respectively. These

are obviously chemically equivalent and the desired factor is

expressed by the fraction (6KMnO\_{4}/5K\_{2}Cr\_{2}O\_{7}) or

(948.0/1471.0).

3. 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, the amount of MnO\_{2}

in a sample of the mineral pyrolusite may be determined by dissolving

the mineral in hydrochloric acid, absorbing the evolved chlorine in a

solution of potassium iodide, and measuring the liberated iodine

by titration with a standard solution of sodium thiosulphate. The

reactions involved are:

MnO\_{2} + 4HCl --> MnCl\_{2} + 2H\_{2}O + Cl\_{2}

Cl\_{2} + 2KI --> I\_{2} + 2KCl

I\_{2} + 2Na\_{2}S\_{2}O\_{3} --> 2NaI + Na\_{2}S\_{4}O\_{6}

Assuming that the weight of thiosulphate corresponding to the

volume of sodium thiosulphate solution used is known, what is the

corresponding weight of manganese dioxide? From the reactions given

above, the following proportions may be stated:

2Na\_{2}S\_{2}O\_{3}:I\_{2} = 316.4:253.9,

I\_{2}:Cl\_{2} = 253.9:71,

Cl\_{2}:MnO\_{2} = 71:86.9.

After canceling the common factors, there remains

2Na\_{2}S\_{2}O\_{3}:MnO\_{2} = 316.4:86.9, and the factor for the

conversion of thiosulphate into an equivalent of manganese dioxide is

86.9/316.4.

4. 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 read

488. 120.0

2(BaCl\_{2}.2H\_{2}O):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.

5. It is sometimes desirable to avoid the manipulation required for

the separation of the constituents of a mixture of substances by

making what is called an "indirect analysis." For example, in the

analysis of silicate rocks, the sodium and potassium present may be

obtained in the form of their chlorides and weighed together. If the

weight of such a mixture is known, and also the percentage of chlorine

present, it is possible to calculate the amount of each chloride in

the mixture. Let it be assumed that the weight of the mixed chlorides

is 0.15 gram, and that it contains 53 per cent of chlorine.

The simplest solution of such a problem is reached through algebraic

methods. The weight of chlorine is evidently 0.15 x 0.53, or 0.0795

gram. Let x represent the weight of sodium chloride present and y

that of potassium chloride. The molecular weight of NaCl is 58.5 and

that of KCl is 74.6. The atomic weight of chlorine is 35.5. Then

x + y = 0.15

(35.5/58.5)x + (35.5/74.6)y = 0.00795

Solving these equations for x shows the weight of NaCl to be 0.0625

gram. The weight of KCl is found by subtracting this from 0.15.

The above is one of the most common types of indirect analyses. Others

are more complex but they can be reduced to algebraic expressions and

solved by their aid. It should, however, be noted that the results

obtained by these indirect methods cannot be depended upon for high

accuracy, since slight errors in the determination of the common

constituent, as chlorine in the above mixture, will cause considerable

variations in the values found for the components. They should not be

employed when direct methods are applicable, if accuracy is essential.

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 195 have been employed, using, however, only the first

decimal but increasing this by 1 when the second decimal is 5 or

above. Thus, 39.1 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.)

VOLUMETRIC ANALYSIS

1. How many grams of pure potassium hydroxide are required for exactly

1 liter of normal alkali solution?

!Answer!: 56.1 grams.

2. Calculate the equivalent in grams (a) of sulphuric acid as an acid;

(b) of hydrochloric acid as an acid; (c) of oxalic acid as an acid;

(d) of nitric acid as an acid.

!Answers!: (a) 49.05; (b) 36.5; (c) 63; (d) 63.

3. Calculate the equivalent in grams of (a) potassium hydroxide;

(b) of sodium carbonate; (c) of barium hydroxide; (d) of sodium

bicarbonate when titrated with an acid.

!Answers!: (a) 56.1; (b) 53.8; (c) 85.7; (d) 84.

4. What is the equivalent in grams of Na\_{2}HPO\_{4} (a) as a

phosphate; (b) as a sodium salt?

!Answers!: (a) 47.33; (b) 71.0.

5. A sample of aqueous hydrochloric acid has a specific gravity

of 1.12 and contains 23.81 per cent hydrochloric acid by weight.

Calculate the grams and the milliequivalents of hydrochloric acid

(HCl) in each cubic centimeter of the aqueous acid.

!Answers!: 0.2667 gram; 7.307 milliequivalents.

6. How many cubic centimeters of hydrochloric acid (sp. gr. 1.20

containing 39.80 per cent HCl by weight) are required to furnish 36.45

grams of the gaseous compound?

!Answer!: 76.33 cc.

7. A given solution contains 0.1063 equivalents of hydrochloric acid

in 976 cc. What is its normal value?

!Answer!: 0.1089 N.

8. In standardizing a hydrochloric acid solution it is found that

47.26 cc. of hydrochloric acid are exactly equivalent to 1.216 grams

of pure sodium carbonate, using methyl orange as an indicator. What is

the normal value of the hydrochloric acid?

!Answer!: 0.4855 N.

9. Convert 42.75 cc. of 0.5162 normal hydrochloric acid to the

equivalent volume of normal hydrochloric acid.

!Answer!: 22.07 cc.

10. A solution containing 25.27 cc. of 0.1065 normal hydrochloric acid

is added to one containing 92.21 cc. of 0.5431 normal sulphuric acid

and 50 cc. of exactly normal potassium hydroxide added from a pipette.

Is the solution acid or alkaline? How many cubic centimeters of

0.1 normal acid or alkali must be added to exactly neutralize the

solution?

!Answer!: 27.6 cc. alkali (solution is acid).

11. By experiment the normal value of a sulphuric acid solution is

found to be 0.5172. Of this acid 39.65 cc. are exactly equivalent to

21.74 cc. of a standard alkali solution. What is the normal value of

the alkali?

!Answer!: 0.9432 N.

12. A solution of sulphuric acid is standardized against a sample of

calcium carbonate which has been previously accurately analyzed and

found to contain 92.44% CaCO\_{3} and no other basic material. The

sample weighing 0.7423 gram was titrated by adding an excess of acid

(42.42 cc.) and titrating the excess with sodium hydroxide solution

(11.22 cc.). 1 cc. of acid is equivalent to 0.9976 cc. of sodium

hydroxide. Calculate the normal value of each.

!Answers!: Acid 0.4398 N; alkali 0.4409 N.

13. Given five 10 cc. portions of 0.1 normal hydrochloric acid, (a)

how many grams of silver chloride will be precipitated by a portion

when an excess of silver nitrate is added? (b) how many grams of pure

anhydrous sodium carbonate (Na\_{2}CO\_{3}) will be neutralized by a

portion of it? (c) how many grams of silver will there be in the

silver chloride formed when an excess of silver nitrate is added to a

portion? (d) how many grams of iron will be dissolved to FeCl\_{2} by a

portion of it? (e) how many grams of magnesium chloride will be formed

and how many grams of carbon dioxide liberated when an excess of

magnesium carbonate is treated with a portion of the acid?

!Answers!: (a) 0.1434; (b) 0.053; (c) 0.1079; (d) 0.0279; (e) 0.04765,

and 0.022.

14. If 30.00 grams of potassium tetroxalate

(KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O) are dissolved and the solution

diluted to exactly 1 liter, and 40 cc. are neutralized with 20 cc.

of a potassium carbonate solution, what is the normal value of the

carbonate solution?

!Answer!: 0.7084 N.

15. How many cubic centimeters of 0.3 normal sulphuric acid will be

required to neutralize (a) 30 cc. of 0.5 normal potassium hydroxide;

(b) to neutralize 30 cc. of 0.5 normal barium hydroxide; (c) to

neutralize 20 cc. of a solution containing 10.02 grams of potassium

bicarbonate per 100 cc.; (d) to give a precipitate of barium sulphate

weighing 0.4320 gram?

!Answers!: (a) 50 cc.; (b) 50 cc.; (c) 66.73 cc.; (d) 12.33 cc.

16. It is desired to dilute a solution of sulphuric acid of which 1

cc. is equivalent to 0.1027 gram of pure sodium carbonate to make it

exactly 1.250 normal. 700 cc. of the solution are available. To what

volume must it be diluted?

!Answer!: 1084 cc.

17. Given the following data: 1 cc. of NaOH = 1.117 cc. HCl. The HCl

is 0.4876 N. How much water must be added to 100 cc. of the alkali to

make it exactly 0.5 N.?

!Answer!: 9.0 cc.

18. What is the normal value of a sulphuric acid solution which has a

specific gravity of 1.839 and contains 95% H\_{2}SO\_{4} by weight?

!Answer!: 35.61 N.

19. A sample of Rochelle Salt (KNaC\_{4}H\_{4}O\_{6}.4H\_{2}O), after

ignition in platinum to convert it to the double carbonate, is

titrated with sulphuric acid, using methyl orange as an indicator.

From the following data calculate the percentage purity of the sample:

Wt. sample = 0.9500 gram

H\_{2}SO\_{4} used = 43.65 cc.

NaOH used = 1.72 cc.

1 cc. H\_{2}SO\_{4} = 1.064 cc. NaOH

Normal value NaOH = 0.1321 N.

!Answer!: 87.72 cc.

20. One gram of a mixture of 50% sodium carbonate and 50% potassium

carbonate is dissolved in water, and 17.36 cc. of 1.075 N acid is

added. Is the resulting solution acid or alkaline? How many cubic

centimeters of 1.075 N acid or alkali will have to be added to make

the solution exactly neutral?

!Answers!: Acid; 1.86 cc. alkali.

21. In preparing an alkaline solution for use in volumetric work, an

analyst, because of shortage of chemicals, mixed exactly 46.32 grams

of pure KOH and 27.64 grams of pure NaOH, and after dissolving in

water, diluted the solution to exactly one liter. How many cubic

centimeters of 1.022 N hydrochloric acid are necessary to neutralize

50 cc. of the basic solution?

!Answer!: 74.18 cc.

22. One gram of crude ammonium salt is treated with strong potassium

hydroxide solution. The ammonia liberated is distilled and collected

in 50 cc. of 0.5 N acid and the excess titrated with 1.55 cc. of 0.5 N

sodium hydroxide. Calculate the percentage of NH\_{3} in the sample.

!Answer!: 41.17%.

23. In titrating solutions of alkali carbonates in the presence of

phenolphthalein, the color change takes place when the carbonate has

been converted to bicarbonate. In the presence of methyl orange, the

color change takes place only when the carbonate has been completely

neutralized. From the following data, calculate the percentages of

Na\_{2}CO\_{3} and NaOH in an impure mixture. Weight of sample, 1.500

grams; HCl (0.5 N) required for phenolphthalein end-point, 28.85 cc.;

HCl (0.5 N) required to complete the titration after adding methyl

orange, 23.85 cc.

!Answers!: 6.67% NaOH; 84.28% Na\_{2}CO\_{3}.

24. A sample of sodium carbonate containing sodium hydroxide weighs

1.179 grams. It is titrated with 0.30 N hydrochloric acid, using

phenolphthalein in cold solution as an indicator and becomes colorless

after the addition of 48.16 cc. Methyl orange is added and 24.08 cc.

are needed for complete neutralization. What is the percentage of NaOH

and Na\_{2}CO\_{3}?

!Answers!: 24.50% NaOH; 64.92% Na\_{2}CO\_{3}.

25. From the following data, calculate the percentages of Na\_{2}CO\_{3}

and NaHCO\_{3} in an impure mixture. Weight of sample 1.000 gram;

volume of 0.25 N hydrochloric acid required for phenolphthalein

end-point, 26.40 cc.; after adding an excess of acid and boiling out

the carbon dioxide, the total volume of 0.25 N hydrochloric acid

required for phenolphthalein end-point, 67.10 cc.

!Answer!: 69.95% Na\_{2}CO\_{3}; 30.02% NaHCO\_{3}.

26. In the analysis of a one-gram sample of soda ash, what must be the

normality of the acid in order that the number of cubic centimeters of

acid used shall represent the percentage of carbon dioxide present?

!Answer!: 0.4544 gram.

27. What weight of pearl ash must be taken for analysis in order that

the number of cubic centimeters of 0.5 N acid used may be equal to one

third the percentage of K\_{2}CO\_{3}?

!Answer!: 1.152 grams.

28. What weight of cream of tartar must have been taken for analysis

in order to have obtained 97.60% KHC\_{4}H\_{4}O\_{6} in an analysis

involving the following data: NaOH used = 30.06 cc.; H\_{2}SO\_{4}

solution used = 0.50 cc.; 1 cc. H\_{2}SO\_{4} sol. = 0.0255 gram

CaCO\_{3}; 1 cc. H\_{2}SO\_{4} sol. = 1.02 cc. NaOH sol.?

!Answer!: 2.846 grams.

29. Calculate the percentage of potassium oxide in an impure sample of

potassium carbonate from the following data: Weight of sample = 1.00

gram; HCl sol. used = 55.90 cc.; NaOH sol. used = 0.42 cc.; 1 cc. NaOH

sol. = 0.008473 gram of KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O; 2 cc.

HCl sol. = 5 cc. NaOH sol.

!Answer!: 65.68%.

30. Calculate the percentage purity of a sample of calcite

(CaCO\_{3}) from the following data: (Standardization); Weight of

H\_{2}C\_{2}O\_{4}.2H\_{2}O = 0.2460 gram; NaOH solution used = 41.03

cc.; HCl solution used = 0.63; 1 cc. NaOH solution = 1.190 cc. HCl

solution. (Analysis); Weight of sample 0.1200 gram; HCl used = 36.38

cc.; NaOH used = 6.20 cc.

!Answer!: 97.97%.

31. It is desired to dilute a solution of hydrochloric acid to exactly

0.05 N. The following data are given: 44.97 cc. of the hydrochloric

acid are equivalent to 43.76 cc. of the NaOH solution. The NaOH

is standardized against a pure potassium tetroxalate

(KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O) weighing 0.2162 gram and

requires 49.14 cc. How many cc. of water must be added to 1000 cc. of

the aqueous hydrochloric acid?

!Answer!: 11 cc.

32. How many cubic centimeters of 3 N phosphoric acid must be added to

300 cc. of 0.4 N phosphoric acid in order that the resulting solution

may be 0.6 N?

!Answer!: 25 cc.

33. To oxidize the iron in 1 gram of

FeSO\_{4}(NH\_{4})\_{2}SO\_{4}.6H\_{2}O (mol. wgt. 392) requires 3 cc. of

a given solution of HNO\_{3}. What is the normality of the nitric

acid when used as an acid? 6FeSO\_{4} + 2HNO\_{3} + 2H\_{2}SO\_{4} =

3Fe\_{2}(SO\_{4})\_{3} + 2NO + 4H\_{2}O.

!Answer!: 0.2835 N.

34. The same volume of carbon dioxide at the same temperature and the

same pressure is liberated from a 1 gram sample of dolomite, by adding

an excess of hydrochloric acid, as can be liberated by the addition of

35 cc. of 0.5 N hydrochloric acid to an excess of any pure or impure

carbonate. Calculate the percentage of CO\_{2} in the dolomite.

!Answer!: 38.5%.

35. How many cubic centimeters of sulphuric acid (sp. gr. 1.84,

containing 96% H\_{2}SO\_{4} by weight) will be required to displace the

chloride in the calcium chloride formed by the action of 100 cc. of

0.1072 N hydrochloric acid on an excess of calcium carbonate, and how

many grams of CaSO\_{4} will be formed?

!Answers!: 0.298 cc.; 0.7300 gram.

36. Potassium hydroxide which has been exposed to the air is found on

analysis to contain 7.62% water, 2.38% K\_{2}CO\_{3}. and 90% KOH. What

weight of residue will be obtained if one gram of this sample is added

to 46 cc. of normal hydrochloric acid and the resulting solution,

after exact neutralization with 1.070 N potassium hydroxide solution,

is evaporated to dryness?

!Answer!: 3.47 grams.

37. A chemist received four different solutions, with the statement

that they contained either pure NaOH; pure Na\_{2}CO\_{3}; pure

NaHCO\_{3}, or mixtures of these substances. From the following data

identify them:

Sample I. On adding phenolphthalein to a solution of the substance, it

gave no color to the solution.

Sample II. On titrating with standard acid, it required 15.26 cc. for

a change in color, using phenolphthalein, and 17.90 cc. additional,

using methyl orange as an indicator.

Sample III. The sample was titrated with hydrochloric acid until the

pink of phenolphthalein disappeared, and on the addition of methyl

orange the solution was colored pink.

Sample IV. On titrating with hydrochloric acid, using phenolphthalein,

15.00 cc. were required. A new sample of the same weight required

exactly 30 cc. of the same acid for neutralization, using methyl

orange.

!Answers!: (a) NaHCO\_{3}; (b) NaHCO\_{3}+Na\_{2}CO\_{3}; (c)NaOH; (d)

Na\_{2}CO\_{3}.

38. In the analysis of a sample of KHC\_{4}H\_{4}O\_{6} the following

data are obtained: Weight sample = 0.4732 gram. NaOH solution used =

24.97 cc. 3.00 cc. NaOH = 1 cc. of H\_{3}PO\_{4} solution of which 1

cc. will precipitate 0.01227 gram of magnesium as MgNH\_{4}PO\_{4}.

Calculate the percentage of KHC\_{4}H\_{4}O\_{6}.

!Answer!: 88.67%.

39. A one-gram sample of sodium hydroxide which has been exposed to

the air for some time, is dissolved in water and diluted to exactly

500 cc. One hundred cubic centimeters of the solution, when titrated

with 0.1062 N hydrochloric acid, using methyl orange as an indicator,

requires 38.60 cc. for complete neutralization. Barium chloride in

excess is added to a second portion of 100 cc. of the solution, which

is diluted to exactly 250 cc., allowed to stand and filtered. Two

hundred cubic centimeters of this filtrate require 29.62 cc. of 0.1062

N hydrochloric acid for neutralization, using phenolphthalein as an

indicator. Calculate percentage of NaOH, Na\_{2}CO\_{3}, and H\_{2}O.

!Answers!: 78.63% NaOH; 4.45% Na\_{2}CO\_{3}; 16.92% H\_{2}O.

40. A sodium hydroxide solution (made from solid NaOH which has been

exposed to the air) was titrated against a standard acid using methyl

orange as an indicator, and was found to be exactly 0.1 N. This

solution was used in the analysis of a material sold at 2 cents per

pound per cent of an acid constituent A, and always mixed so that

it was supposed to contain 15% of A, on the basis of the analyst's

report. Owing to the carelessness of the analyst's assistant, the

sodium hydroxide solution was used with phenolphthalein as an

indicator in cold solution in making the analyses. The concern

manufacturing this material sells 600 tons per year, and when the

mistake was discovered it was estimated that at the end of a year

the error in the use of indicators would either cost them or their

customers $6000. Who would lose and why? Assuming the impure NaOH used

originally in making the titrating solution consisted of NaOH and

Na\_{2}CO\_{3} only, what per cent of each was present?

!Answers!: Customer lost; 3.94% Na\_{2}CO\_{3}; 96.06% NaOH.

41. In the standardization of a K\_{2}Cr\_{2}O\_{7} solution against iron

wire, 99.85% pure, 42.42 cc. of the solution were added. The weight of

the wire used was 0.22 gram. 3.27 cc. of a ferrous sulphate solution

having a normal value as a reducing agent of 0.1011 were added

to complete the titration. Calculate the normal value of the

K\_{2}Cr\_{2}O\_{7}.

!Answer!: 0.1006 N.

42. What weight of iron ore containing 56.2% Fe should be taken to

standardize an approximately 0.1 N oxidizing solution, if not more

than 47 cc. are to be used?

!Answer!: 0.4667 gram.

43. One tenth gram of iron wire, 99.78% pure, is dissolved in

hydrochloric acid and the iron oxidized completely with bromine water.

How many grams of stannous chloride are there in a liter of solution

if it requires 9.47 cc. to just reduce the iron in the above? What

is the normal value of the stannous chloride solution as a reducing

agent?

!Answer!: 17.92 grams; 0.1888 N.

44. One gram of an oxide of iron is fused with potassium acid sulphate

and the fusion dissolved in acid. The iron is reduced with stannous

chloride, mercuric chloride is added, and the iron titrated with a

normal K\_{2}Cr\_{2}O\_{7} solution. 12.94 cc. were used. What is the

formula of the oxide, FeO, Fe\_{2}O\_{3}, or Fe\_{3}O\_{4}?

!Answer!: Fe\_{3}O\_{4}.

45. If an element has 98 for its atomic weight, and after reduction

with stannous chloride could be oxidized by bichromate to a state

corresponding to an XO\_{4}^{-} anion, compute the oxide, or valence,

corresponding to the reduced state from the following data: 0.3266

gram of the pure element, after being dissolved, was reduced with

stannous chloride and oxidized by 40 cc. of K\_{2}Cr\_{2}O\_{7}, of which

one cc. = 0.1960 gram of FeSO\_{4}(NH\_{4})\_{2}SO\_{4}.6H\_{2}O.

!Answer!: Monovalent.

46. Determine the percentage of iron in a sample of limonite from the

following data: Sample = 0.5000 gram. KMnO\_{4} used = 50 cc. 1 cc.

KMnO\_{4} = 0.005317 gram Fe. FeSO\_{4} used = 6 cc. 1 cc. FeSO\_{4} =

0.009200 gram FeO.

!Answer!: 44.60%.

47. If 1 gram of a silicate yields 0.5000 gram of Fe\_{2}O\_{3} and

Al\_{2}O\_{3} and the iron present requires 25 cc. of 0.2 N KMnO\_{4},

calculate the percentage of FeO and Al\_{2}O\_{3} in the sample.

!Answer!: 35.89% FeO; 10.03% Al\_{2}O\_{3}.

48. A sample of magnesia limestone has the following composition:

Silica, 3.00%; ferric oxide and alumina, 0.20%; calcium oxide, 33.10%;

magnesium oxide, 20.70%; carbon dioxide, 43.00%. In manufacturing lime

from the above the carbon dioxide is reduced to 3.00%. How many cubic

centimeters of normal KMnO\_{4} will be required to determine the

calcium oxide volumetrically in a 1 gram sample of the lime?

!Answer!: 20.08 cc.

49. If 100 cc. of potassium bichromate solution (10 gram

K\_{2}Cr\_{2}O\_{7} per liter), 5 cc. of 6 N sulphuric acid, and 75 cc.

of ferrous sulphate solution (80 grams FeSO\_{4}.7H\_{2}O per liter) are

mixed, and the resulting solution titrated with 0.2121 N KMnO\_{4}, how

many cubic centimeters of the KMnO\_{4} solution will be required to

oxidize the iron?

!Answer!: 5.70 cc.

50. If a 0.5000 gram sample of limonite containing 59.50 per cent

Fe\_{2}O\_{3} requires 40 cc. of KMnO\_{4} to oxidize the iron, what

is the value of 1 cc. of the permanganate in terms of (a) Fe, (b)

H\_{2}C\_{2}O\_{4}.2H\_{2}O?

!Answers!: (a) 0.005189 gram; (b) 0.005859 gram.

51. A sample of pyrolusite weighing 0.6000 gram is treated with 0.9000

gram of oxalic acid. The excess oxalic acid requires 23.95 cc. of

permanganate (1 cc. = 0.03038 gram FeSO\_{4}.7H\_{2}O). What is the

percentage of MnO\_{2}, in the sample?

!Answer!: 84.47%.

52. A solution contains 50 grams of

KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O per liter. What is the normal

value of the solution (a) as an acid, and (b) as a reducing agent?

!Answers!: (a) 0.5903 N; (b) 0.7872 N.

53. In the analysis of an iron ore containing 60% Fe\_{2}O\_{3}, a

sample weighing 0.5000 gram is taken and the iron is reduced with

sulphurous acid. On account of failure to boil out all the excess

SO\_{2}, 38.60 cubic centimeters of 0.1 N KMnO\_{4} were required to

titrate the solution. What was the error, percentage error, and what

weight of sulphur dioxide was in the solution?

!Answers!: (a) 1.60%; (b) 2.67%; (c) 0.00322 gram.

54. From the following data, calculate the ratio of the nitric acid as

an oxidizing agent to the tetroxalate solution as a reducing agent:

1 cc. HNO\_{3} = 1.246 cc. NaOH solution; 1 cc. NaOH = 1.743 cc.

KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O solution; Normal value NaOH =

0.12.

!Answer!: 4.885.

55. Given the following data: 25 cc. of a hydrochloric acid, when

standardized gravimetrically as silver chloride, yields a precipitate

weighing 0.5465 gram. 24.35 cc. of the hydrochloric acid are exactly

equivalent to 30.17 cc. of KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O

solution. How much water must be added to a liter of the oxalate

solution to make it exactly 0.025 N as a reducing agent?

!Answer!: 5564 cc.

56. Ten grams of a mixture of pure potassium tetroxalate

(KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O) and pure oxalic acid

(H\_{2}C\_{2}O\_{4}.2H\_{2}O) are dissolved in water and diluted to

exactly 1000 cc. The normal value of the oxalate solution when used as

an acid is 0.1315. Calculate the ratio of tetroxalate to oxalate used

in making up the solution and the normal value of the solution as a

reducing agent.

!Answers!: 2:1; 0.1577 N.

57. A student standardized a solution of NaOH and one of KMnO\_{4}

against pure KHC\_{2}O\_{4}.H\_{2}C\_{2}O\_{4}.2H\_{2}O and found the former

to be 0.07500 N as an alkali and the latter exactly 0.1 N as an

oxidizing agent. By coincidence, exactly 47.26 cc. were used in each

standardization. Find the ratio of the oxalate used in the

NaOH standardization to the oxalate used in the permanganate

standardization.

!Answer!: 1:1.

58. A sample of apatite weighing 0.60 gram is analyzed for its

phosphoric anhydride content. If the phosphate is precipitated as

(NH\_{4})\_{3}PO\_{4}.12MoO\_{3}, and the precipitate (after solution and

reduction of the MoO\_{3} to Mo\_{24}O\_{37}), requires 100 cc. of normal

KMnO\_{4} to oxidize it back to MoO\_{3}, what is the percentage of

P\_{2}O\_{5}?

!Answer!: 33.81%.

59. In the analysis of a sample of steel weighing 1.881 grams the

phosphorus was precipitated with ammonium molybdate and the yellow

precipitate was dissolved, reduced and titrated with KMnO\_{4}. If the

sample contained 0.025 per cent P and 6.01 cc. of KMnO\_{4} were used,

to what oxide was the molybdenum reduced? 1 cc. KMnO\_{4} = 0.007188

gram Na\_{2}C\_{2}O\_{4}.

!Answer!: Mo\_{4}O\_{5}.

60. What is the value of 1 cc. of an iodine solution (1 cc. equivalent

to 0.0300 gram Na\_{2}S\_{2}O\_{3}) in terms of As\_{2}O\_{3}?

!Answer!: 0.009385 gram.

61. 48 cc. of a solution of sodium thiosulphate are required to

titrate the iodine liberated from an excess of potassium iodide

solution by 0.3000 gram of pure KIO\_{3}. (KIO\_{3} + 5KI + 3H\_{2}SO\_{4}

= 3K\_{2}SO\_{4} + 3I\_{2} + 3H\_{2}O.) What is the normal strength of the

sodium thiosulphate and the value of 1 cc. of it in terms of iodine?

!Answers!: 0.1753 N; 0.02224 gram.

62. One thousand cubic centimeters of 0.1079 N sodium thiosulphate

solution is allowed to stand. One per cent by weight of the

thiosulphate is decomposed by the carbonic acid present in the

solution. To what volume must the solution be diluted to make it

exactly 0.1 N as a reducing agent? (Na\_{2}S\_{2}O\_{3} + 2H\_{2}CO\_{3} =

H\_{2}SO\_{3} + 2NaHCO\_{3} + S.)

!Answer!: 1090 cc.

63. An analyzed sample of stibnite containing 70.05% Sb is given for

analysis. A student titrates it with a solution of iodine of which 1

cc. is equivalent to 0.004950 gram of As\_{2}O\_{3}. Due to an error on

his part in standardization, the student's analysis shows the sample

to contain 70.32% Sb. Calculate the true normal value of the iodine

solution, and the percentage error in the analysis.

!Answers!: 0.1000 N; 0.39%.

64. A sample of pyrolusite weighing 0.5000 gram is treated with an

excess of hydrochloric acid, the liberated chlorine is passed into

potassium iodide and the liberated iodine is titrated with sodium

thiosulphate solution (49.66 grams of pure Na\_{2}S\_{2}O\_{3}.5H\_{2}O

per liter). If 38.72 cc. are required, what volume of 0.25 normal

permanganate solution will be required in an indirect determination

in which a similar sample is reduced with 0.9012 gram

H\_{2}C\_{2}O\_{4}.2H\_{2}O and the excess oxalic acid titrated?

!Answer!: 26.22 cc.

65. In the determination of sulphur in steel by evolving the sulphur

as hydrogen sulphide, precipitating cadmium sulphide by passing the

liberated hydrogen sulphide through ammoniacal cadmium chloride

solution, and decomposing the CdS with acid in the presence of a

measured amount of standard iodine, the following data are obtained:

Sample, 5.027 grams; cc. Na\_{2}S\_{2}O\_{3} sol. = 12.68; cc. Iodine

sol. = 15.59; 1 cc. Iodine sol. = 1.086 cc. Na\_{2}S\_{2}O\_{3} sol.; 1

cc. Na\_{2}S\_{2}O\_{3}= 0.005044 gram Cu. Calculate the percentage of

sulphur. (H\_{2}S + I\_{2} = 2HI + S.)

!Answer!: 0.107%.

66. Given the following data, calculate the percentage of iron in

a sample of crude ferric chloride weighing 1.000 gram. The iodine

liberated by the reaction 2FeCl\_{3}+ 2HI = 2HCl + 2FeCl\_{2} + I\_{2} is

reduced by the addition of 50 cc. of sodium thiosulphate solution and

the excess thiosulphate is titrated with standard iodine and requires

7.85 cc. 45 cc. I\_{2} solution = 45.95 cc. Na\_{2}S\_{2}O\_{3} solution;

45 cc. As\_{2}O\_{3} solution = 45.27 cc. I\_{2} solution. 1 cc. arsenite

solution = 0.005160 gram As\_{2}O\_{3}.

!Answer!: 23.77%.

67. Sulphide sulphur was determined in a sample of reduced barium

sulphate by the evolution method, in which the sulphur was evolved as

hydrogen sulphide and was passed into CdCl\_{2} solution, the acidified

precipitate being titrated with iodine and thiosulphate. Sample, 5.076

grams; cc. I\_{2} = 20.83; cc. Na\_{2}S\_{2}O\_{3} = 12.37; 43.45 cc.

Na\_{2}S\_{2}O\_{3} = 43.42 cc. I\_{2}; 8.06 cc. KMnO\_{4} = 44.66 cc.

Na\_{2}S\_{2}O\_{3}; 28.87 cc. KMnO\_{4} = 0.2004 gram Na\_{2}C\_{2}O\_{4}.

Calculate the percentage of sulphide sulphur in the sample.

!Answer!: 0.050%.

68. What weight of pyrolusite containing 89.21% MnO\_{2} will oxidize

the same amount of oxalic acid as 37.12 cc. of a permanganate

solution, of which 1 cc. will liberate 0.0175 gram of I\_{2} from KI?

!Answer!: 0.2493 gram.

69. A sample of pyrolusite weighs 0.2400 gram and is 92.50% pure

MnO\_{2}. The iodine liberated from KI by the manganese dioxide is

sufficient to react with 46.24 cc. of Na\_{2}S\_{2}O\_{3} sol. What is

the normal value of the thiosulphate?

!Answer!:: 0.1105 N.

70. In the volumetric analysis of silver coin (90% Ag), using a

0.5000 gram sample, what is the least normal value that a potassium

thiocyanate solution may have and not require more than 50 cc. of

solution in the analysis?

!Answer!: 0.08339 N.

71. A mixture of pure lithium chloride and barium bromide weighing

0.6 gram is treated with 45.15 cubic centimeters of 0.2017 N silver

nitrate, and the excess titrated with 25 cc. of 0.1 N KSCN solution,

using ferric alum as an indicator. Calculate the percentage of bromine

in the sample.

!Answer!: 40.11%.

72. A mixture of the chlorides of sodium and potassium from 0.5000

gram of a feldspar weighs 0.1500 gram, and after solution in water

requires 22.71 cc. of 0.1012 N silver nitrate for the precipitation of

the chloride ions. What are the percentages of Na\_{2}O and K\_{2}O in

the feldspar?

!Answer!: 8.24% Na\_{2}O; 9.14% K\_{2}O.

GRAVIMETRIC ANALYSIS

73. Calculate (a) the grams of silver in one gram of silver chloride;

(b) the grams of carbon dioxide liberated by the addition of an excess

of acid to one gram of calcium carbonate; (c) the grams of MgCl\_{2}

necessary to precipitate 1 gram of MgNH\_{4}PO\_{4}.

!Answers!: (a) 0.7526; (b) 0.4397; (c) 0.6940.

74. Calculate the chemical factor for (a) Sn in SnO\_{2}; (b) MgO

in Mg\_{2}P\_{2}O\_{7}; (c) P\_{2}O\_{5} in Mg\_{2}P\_{2}O\_{7}; (d) Fe in

Fe\_{2}O\_{3}; (e) SO\_{4} in BaSO\_{4}.

!Answers!: (a) 0.7879; (b) 0.3620; (c) 0.6378; (d) 0.6990; (e) 0.4115.

75. Calculate the log factor for (a) Pb in PbCrO\_{4}; (b) Cr\_{2}O\_{3}

in PbCrO\_{4}; (c) Pb in PbO\_{2} and (d) CaO in CaC\_{2}O\_{4}.

!Answers!: (a) 9.8069-10, (b) 9.3713-10; (c) 9.9376-10; (d) 9.6415-10.

76. How many grams of Mn\_{3}O\_{4} can be obtained from 1 gram of

MnO\_{2}?

!Answer!: 0.8774 gram.

77. If a sample of silver coin weighing 0.2500 gram gives a

precipitate of AgCl weighing 0.2991 gram, what weight of AgI could

have been obtained from the same weight of sample, and what is the

percentage of silver in the coin?

!Answers!: 0.4898 gr.; 90.05%.

78. How many cubic centimeters of hydrochloric acid (sp. gr. 1.13

containing 25.75% HCl by weight) are required to exactly neutralize

25 cc. of ammonium hydroxide (sp. gr. .90 containing 28.33% NH\_{3} by

weight)?

!Answer!: 47.03 cc.

79. How many cubic centimeters of ammonium hydroxide solution (sp. gr.

0.96 containing 9.91% NH\_{3} by weight) are required to precipitate

the aluminium as aluminium hydroxide from a two-gram sample of alum

(KAl(SO\_{4})\_{2}.12H\_{2}O)? What will be the weight of the ignited

precipitate?

!Answers!: 2.26 cc.; 0.2154 gram.

80. What volume of nitric acid (sp. gr. 1.05 containing 9.0%

HNO\_{3} by weight) is required to oxidize the iron in one gram of

FeSO\_{4}.7H\_{2}O in the presence of sulphuric acid? 6FeSO\_{4} +

2HNO\_{3} + 3H\_{2}SO\_{4} = 3Fe\_{2}(SO\_{4})\_{3} + 2NO + 4H\_{2}O.

!Answer!: 0.80 cc.

81. If 0.7530 gram of ferric nitrate (Fe(NO\_{3})\_{3}.9H\_{2}O) is

dissolved in water and 1.37 cc. of HCl (sp. gr. 1.11 containing 21.92%

HCl by weight) is added, how many cubic centimeters of ammonia (sp.

gr. 0.96 containing 9.91% NH\_{3} by weight) are required to neutralize

the acid and precipitate the iron as ferric hydroxide?

!Answer!: 2.63 cc.

82. To a suspension of 0.3100 gram of Al(OH)\_{3} in water are added

13.00 cc. of aqueous ammonia (sp. gr. 0.90 containing 28.4% NH\_{3} by

weight). How many cubic centimeters of sulphuric acid (sp. gr. 1.18

containing 24.7% H\_{2}SO\_{4} by weight) must be added to the mixture

in order to bring the aluminium into solution?

!Answer!: 34.8 cc.

83. How many cubic centimeters of sulphurous acid (sp. gr. 1.04

containing 75 grams SO\_{2} per liter) are required to reduce the

iron in 1 gram of ferric alum (KFe(SO\_{4})\_{2}.12H\_{2}O)?

Fe\_{2}(SO\_{4})\_{3} + SO\_{2} + 2H\_{2}O = 2FeSO\_{4} + 2H\_{2}SO\_{4}.

!Answer!: 0.85 cc.

84. How many cubic centimeters of a solution of potassium bichromate

containing 26.30 grams of K\_{2}Cr\_{2}O\_{7} per liter must be taken

in order to yield 0.6033 gram of Cr\_{2}O\_{3} after reduction and

precipitation of the chromium?

K\_{2}Cr\_{2}O\_{7} + 3SO\_{2} + H\_{2}SO\_{4} = K\_{2}SO\_{4} +

Cr\_{2}(SO\_{4})\_{3} + H\_{2}O.

!Answer!: 44.39 cc.

85. How many cubic centimeters of ammonium hydroxide (sp. gr. 0.946

containing 13.88% NH\_{3} by weight) are required to precipitate

the iron as Fe(OH)\_{3} from a sample of pure

FeSO\_{4}.(NH\_{4})\_{2}SO\_{4}.6H\_{2}O, which requires 0.34 cc. of nitric

acid (sp. gr. 1.350 containing 55.79% HNO\_{3} by weight) for oxidation

of the iron? (See problem No. 80 for reaction.)

!Answer!: 4.74 cc.

86. In the analysis of an iron ore by solution, oxidation and

precipitation of the iron as Fe(OH)\_{3}, what weight of sample must be

taken for analysis so that each one hundredth of a gram of the ignited

precipitate of Fe\_{2}O\_{3} shall represent one tenth of one per cent

of iron?

!Answer!: 6.99 grams.

87. What weight in grams of impure ferrous ammonium sulphate should

be taken for analysis so that the number of centigrams of BaSO\_{4}

obtained will represent five times the percentage of sulphur in the

sample?

!Answer!: 0.6870 gram.

88. What weight of magnetite must be taken for analysis in order that,

after precipitating and igniting all the iron to Fe\_{2}O\_{3}, the

percentage of Fe\_{2}O\_{4} in the sample may be found by multiplying

the weight in grams of the ignited precipitate by 100?

!Answer!: 0.9665 gram.

89. After oxidizing the arsenic in 0.5000 gram of pure As\_{2}S\_{3} to

arsenic acid, it is precipitated with "magnesia mixture" (MgCl\_{2} +

2NH\_{4}Cl). If exactly 12.6 cc. of the mixture are required, how many

grams of MgCl\_{2} per liter does the solution contain? H\_{3}AsO\_{4} +

MgCl\_{2} + 3NH\_{4}OH = MgNH\_{4}AsO\_{4} + 2NH\_{4}Cl + 3H\_{2}O.

!Answer!: 30.71 grams.

90. A sample is prepared for student analysis by mixing pure apatite

(Ca\_{3}(PO\_{4})\_{2}.CaCl\_{2}) with an inert material. If 1 gram of

the sample gives 0.4013 gram of Mg\_{2}P\_{2}O\_{7}, how many cubic

centimeters of ammonium oxalate solution (containing 40 grams of

(NH\_{4})\_{2}C\_{2}O\_{4}.H\_{2}O per liter) would be required to

precipitate the calcium from the same weight of sample?

!Answer!: 25.60 cc.

91. If 0.6742 gram of a mixture of pure magnesium carbonate and pure

calcium carbonate, when treated with an excess of hydrochloric acid,

yields 0.3117 gram of carbon dioxide, calculate the percentage of

magnesium oxide and of calcium oxide in the sample.

!Answers!: 13.22% MgO; 40.54% CaO. 92. The calcium in a sample of

dolomite weighing 0.9380 gram is precipitated as calcium oxalate and

ignited to calcium oxide. What volume of gas, measured over water

at 20°C. and 765 mm. pressure, is given off during ignition, if the

resulting oxide weighs 0.2606 gram? (G.M.V. = 22.4 liters; V.P. water

at 20°C. = 17.4 mm.)

!Answer!: 227 cc.

93. A limestone is found to contain 93.05% CaCO\_{3}, and 5.16 %

MgCO\_{3}. Calculate the weight of CaO obtainable from 3 tons of the

limestone, assuming complete conversion to oxide. What weight of

Mg\_{2}P\_{2}O\_{7} could be obtained from a 3-gram sample of the

limestone?

!Answers!: 1.565 tons; 0.2044 gram.

94. A sample of dolomite is analyzed for calcium by precipitating

as the oxalate and igniting the precipitate. The ignited product is

assumed to be CaO and the analyst reports 29.50% Ca in the sample.

Owing to insufficient ignition, the product actually contained 8% of

its weight of CaCO\_{3}. What is the correct percentage of calcium in

the sample, and what is the percentage error?

!Answers!: 28.46%; 3.65% error.

95. What weight of impure calcite (CaCO\_{3}) should be taken for

analysis so that the volume in cubic centimeters of CO\_{2} obtained by

treating with acid, measured dry at 18°C. and 763 mm., shall equal the

percentage of CaO in the sample?

!Answer!: 0.2359 gram.

96. How many cubic centimeters of HNO\_{3} (sp. gr. 1.13 containing

21.0% HNO\_{3} by weight) are required to dissolve 5 grams of brass,

containing 0.61% Pb, 24.39% Zn, and 75% Cu, assuming reduction of the

nitric acid to NO by each constituent? What fraction of this volume of

acid is used for oxidation?

!Answers!: 55.06 cc.; 25%.

97. What weight of metallic copper will be deposited from a cupric

salt solution by a current of 1.5 amperes during a period of 45

minutes, assuming 100% current efficiency? (1 Faraday = 96,500

coulombs.)

!Answer!: 1.335 grams.

98. In the electrolysis of a 0.8000 gram sample of brass, there is

obtained 0.0030 gram of PbO\_{2}, and a deposit of metallic copper

exactly equal in weight to the ignited precipitate of Zn\_{2}P\_{2}O\_{7}

subsequently obtained from the solution. What is the percentage

composition of the brass?

!Answers!: 69.75% Cu; 29.92% Zn; 0.33% Pb.

99. A sample of brass (68.90% Cu; 1.10% Pb and 30.00% Zn) weighing

0.9400 gram is dissolved in nitric acid. The lead is determined by

weighing as PbSO\_{4}, the copper by electrolysis and the zinc by

precipitation with (NH\_{4})\_{2}HPO\_{4} in a neutral solution.

(a) Calculate the cubic centimeters of nitric acid (sp. gr. 1.42

containing 69.90% HNO\_{3} by weight) required to just dissolve the

brass, assuming reduction to NO.

!Answer!: 2.48 cc.

(b) Calculate the cubic centimeters of sulphuric acid (sp. gr. 1.84

containing 94% H\_{2}SO\_{4} by weight) to displace the nitric acid.

!Answer!: 0.83 cc.

(c) Calculate the weight of PbSO\_{4}.

!Answer!: 0.0152 gram.

(d) The clean electrode weighs 10.9640 grams. Calculate the weight

after the copper has been deposited.

!Answer!: 11.6116 grams.

(e) Calculate the grams of (NH\_{4})\_{2}HPO\_{4} required to precipitate

the zinc as ZnNH\_{4}PO\_{4}.

!Answer!: 0.5705 gram.

(f) Calculate the weight of ignited Zn\_{2}P\_{2}O\_{7}.

!Answer!: 0.6573 gram.

100. If in the analysis of a brass containing 28.00% zinc an error is

made in weighing a 2.5 gram portion by which 0.001 gram too much is

weighed out, what percentage error in the zinc determination would

result? What volume of a solution of sodium hydrogen phosphate,

containing 90 grams of Na\_{2}HPO\_{4}.12H\_{2}O per liter, would be

required to precipitate the zinc as ZnNH\_{4}PO\_{4} and what weight of

precipitate would be obtained?

!Answers!: (a) 0.04% error; (b) 39.97 cc.; (c) 1.909 grams.

101. A sample of magnesium carbonate, contaminated with SiO\_{2} as its

only impurity, weighs 0.5000 gram and loses 0.1000 gram on ignition.

What volume of disodium phosphate solution (containing 90 grams

Na\_{2}HPO\_{4}.12H\_{2}O per liter) will be required to precipitate the

magnesium as magnesium ammonium phosphate?

!Answer!: 9.07 cc.

102. 2.62 cubic centimeters of nitric acid (sp. gr. 1.42 containing

69.80% HNO\_{2} by weight) are required to just dissolve a sample

of brass containing 69.27% Cu; 0.05% Pb; 0.07% Fe; and 30.61% Zn.

Assuming the acid used as oxidizing agent was reduced to NO in every

case, calculate the weight of the brass and the cubic centimeters of

acid used as acid.

!Answer!: 0.992 gram; 1.97 cc.

103. One gram of a mixture of silver chloride and silver bromide is

found to contain 0.6635 gram of silver. What is the percentage of

bromine?

!Answer!: 21.30%.

104. A precipitate of silver chloride and silver bromide weighs 0.8132

gram. On heating in a current of chlorine, the silver bromide is

converted to silver chloride, and the mixture loses 0.1450 gram

in weight. Calculate the percentage of chlorine in the original

precipitate.

!Answer!: 6.13%.

105. A sample of feldspar weighing 1.000 gram is fused and the silica

determined. The weight of silica is 0.6460 gram. This is fused with 4

grams of sodium carbonate. How many grams of the carbonate actually

combined with the silica in fusion, and what was the loss in weight

due to carbon dioxide during the fusion?

!Answers!: 1.135 grams; 0.4715 gram.

106. A mixture of barium oxide and calcium oxide weighing 2.2120 grams

is transformed into mixed sulphates, weighing 5.023 grams. Calculate

the grams of calcium oxide and barium oxide in the mixture.

!Answers!: 1.824 grams CaO; 0.3877 gram BaO.

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

dissociated 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 tenth-normal solutions at a temperature of about 18°C.

ACIDS

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SUBSTANCE | PERCENTAGE DISSOCIATION IN

| 0.1 EQUIVALENT SOLUTION

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|

HCl, HBr, HI, HNO\_{3} | 90

|

HClO\_{3}, HClO\_{4}, HMnO\_{4} | 90

|

H\_{2}SO\_{4} <--> H^{+} + HSO\_{4}^{-} | 90

|

H\_{2}C\_{2}O\_{4} <--> H^{+} + HC\_{2}O\_{4}^{-} | 50

|

H\_{2}SO\_{3} <--> H^{+} + HSO{\_}3^{-} | 20

|

H\_{3}PO\_{4} <--> H^{+} + H\_{2}PO\_{4}^{-} | 27

|

H\_{2}PO\_{4}^{-} <--> H^{+} + HPO\_{4}^{--} | 0.2

|

H\_{3}AsO\_{4} <--> H^{+} + H\_{2}AsO\_{4}^{-} | 20

|

HF | 9

|

HC\_{2}H\_{3}O\_{2} | 1.4

|

H\_{2}CO\_{3} <--> H^{+} + HCO\_{3}^{-} | 0.12

|

H\_{2}S <--> H^{+} + HS^{-} | 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

|

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SALTS

=========================================================================

|

TYPE OF SALT | PERCENTAGE DISSOCIATION IN

| 0.1 EQUIVALENT SOLUTION

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

|

R^{+}R^{-} | 86

|

R^{++}(R^{-})\_{2} | 72

|

(R^{+})\_{2}R^{--} | 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,

!i.e.!, HC\_{2}H\_{3}O\_{2} <--> H^{+} + C\_{2}H\_{3}O\_{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\_{2}H\_{3}O\_{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:

(!Conc'n H^{+} x Conc'n C\_{2}H\_{3}O\_{2}^{-})/Conc'n HC\_{2}H\_{3}O\_{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 temperature 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 of about

18°C.[1]

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| | | |

MOLAL | FRACTION | MOLAL CONCENTRA- | MOLAL CONCENTRA- | VALUE OF

CONCENTRATION | IONIZED | TION OF H^{+} AND| TION OF UNDIS- | CONSTANT

CONSTANT | | ACETATE^{-} IONS | SOCIATED ACID |

\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_

| | | |

1.0 | .004 | .004 | .996 | .0000161

| | | |

0.1 | .013 | .0013 | .0987 | .0000171

| | | |

0.01 | .0407 | .000407 | .009593 | .0000172

| | | |

===========================================================================

[Footnote 1: Alexander Smith, !General Inorganic Chemistry!, p. 579.]

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\_{2}H\_{3}O\_{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 (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\_{2}H\_{3}O\_{2} <--> H^{+} + C\_{2}H\_{3}O\_{2}^{-}, will proceed from

left to 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 re-establish 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 equilbrium,

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} <-->

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 quantitative

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:

(!Conc'n Ag^{+} x 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

constant for that temperature. Since it is a constant, it may be

eliminated, and the expression becomes !Conc'n Ag^{+} x 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 readily be 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 2 on page 113.

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:

(!(Conc'n H^{+})^{2} x Conc'n S^{--})/Conc'n H\_{2}S = 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\_{2}S. 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 minute quantity of dissolved hydroxide dissociates thus:

Mg(OH)\_{2} <--> 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\_{2}O\_{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\_{2}O\_{4}^{--} ions lessens and more CaC\_{2}O\_{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 10^{7} 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\_{2}O <--> 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\_{2}S 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. The solution exhibits an acid reaction.

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 32.)

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 below 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 other common elements. For a more extended

discussion of this topic the student should refer to other treatises.

POTENTIAL SERIES OF THE METALS

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

| | |

| POTENTIAL | | POTENTIAL

| IN VOLTS | | IN VOLTS

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_

| | |

Sodium Na^{+} | +2.44 | Lead Pb^{++} | -0.13

Calcium Ca^{++} | | Hydrogen H^{+} | -0.28

Magnesium Mg^{++} | | Bismuth Bi^{+++}|

Aluminum A1^{+++} | +1.00 | Antimony | -0.75

Manganese Mn^{++} | | Arsenic |

Zinc Zn^{++} | +0.49 | Copper Cu^{++} | -0.61

Cadmium Cd^{++} | +0.14 | Mercury Hg^{+} | -1.03

Iron Fe^{++} | +0.063 | Silver Ag^{+} | -1.05

Cobalt Co^{++} | -0.045 | Platinum |

Nickel Ni^{++} | -0.049 | Gold |

Tin Sn^{++} | -0.085(?) | |

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_

THE FOLDING OF A FILTER PAPER

If a filter paper is folded along its diameter, and again folded along

the radius at right angles to the original fold, a cone is formed on

opening, the angle of which is 60°. Funnels for analytical use are

supposed to have the same angle, but are rarely accurate. It is

possible, however, with care, to fit a filter thus folded into a

funnel in such a way as to prevent air from passing down between the

paper and the funnel to break the column of liquid in the stem,

which aids greatly, by its gentle suction, in promoting the rate of

filtration.

Such a filter has, however, the disadvantage that there are three

thicknesses of paper back of half of its filtering surface, as a

consequence of which one half of a precipitate washes or drains more

slowly. Much time may be saved in the aggregate by learning to fold a

filter in such a way as to improve its effective filtering surface.

The directions which follow, though apparently complicated on first

reading, are easily applied and easily remembered. Use a 6-inch filter

for practice. Place four dots on the filter, two each on diameters

which are at right angles to each other. Then proceed as follows:

(1) Fold the filter evenly across one of the diameters, creasing it

carefully; (2) open the paper, turn it over, rotate it 90° to the

right, bring the edges together and crease along the other diameter;

(3) open, and rotate 45° to the right, bring edges together, and

crease evenly; (4) open, and rotate 90° to the right, and crease

evenly; (5) open, turn the filter over, rotate 22-(1/2)° to the right,

and crease evenly; (6) open, rotate 45° to the right and crease

evenly; (7) open, rotate 45° to the right and crease evenly; (8) open,

rotate 45° to the right and crease evenly; (9) open the filter, and,

starting with one of the dots between thumb and forefinger of the

right hand, fold the second crease to the left over on it, and do

the same with each of the other dots. Place it, thus folded, in the

funnel, moisten it, and fit to the side of the funnel. The filter will

then have four short segments where there are three thicknesses

and four where there is one thickness, but the latter are evenly

distributed around its circumference, thus greatly aiding the passage

of liquids through the paper and hastening both filtration and washing

of the whole contents of the filter.

!SAMPLE PAGES FOR LABORATORY RECORDS!

!Page A!

Date

CALIBRATION OF BURETTE No.

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

| | | |

BURETTE | DIFFERENCE | OBSERVED | DIFFERENCE | CALCULATED

READINGS | | WEIGHTS | | CORRECTION

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_

0.02 | | 16.27 | |

10.12 | 10.10 | 26.35 | 10.08 | -.02

20.09 | 9.97 | 36.26 | 9.91 | -.06

30.16 | 10.07 | 46.34 | 10.08 | +.01

40.19 | 10.03 | 56.31 | 9.97 | -.06

50.00 | 9.81 | 66.17 | 9.86 | +.05

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_

These data to be obtained in duplicate for each burette.

!Page B!

Date

DETERMINATION OF COMPARATIVE STRENGTH HCl vs. NaOH

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

| |

DETERMINATION | I | II

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

| |

| Corrected | Corrected

Final Reading HCl | 48.17 48.08 | 43.20 43.14

Initial Reading HCl | 0.12 .12 | .17 .17

| ----- ----- | ----- -----

| 47.96 | 42.97

| |

| Corrected | Corrected

Final Reading HCl | 46.36 46.29 | 40.51 40.37

Initial Reading HCl | 1.75 1.75 | .50 .50

| ----- ----- | ----- -----

| 44.54 | 39.87

| |

log cc. NaOH | 1.6468 | 1.6008

colog cc. HCl | 8.3192 | 8.3668

| ------ | ------

| 9.9680 - 10 | 9.9676 - 10

1 cc. HCl | .9290 cc. NaOH | .9282 cc. NaOH

Mean | .9286 |

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Signed

!Page C!

Date

STANDARDIZATION OF HYDROCHLORIC ACID

=====================================================================

| |

Weight sample and tube| 9.1793 | 8.1731

| 8.1731 | 6.9187

| ------ | ------

Weight sample | 1.0062 | 1.2544

| |

Final Reading HCl | 39.97 39.83 | 49.90 49.77

Initial Reading HCl | .00 .00 | .04 .04

| ----- ----- | ----- -----

| 39.83 | 49.73

| |

Final Reading NaOH | .26 .26 | .67 .67

Initial Reading NaOH | .12 .12 | .36 .36

| --- --- | --- ---

| .14 | .31

| |

| .14 | .31

Corrected cc. HCl | 39.83 - ----- = 39.68 | 49.73 - ----- = 49.40

| .9286 | .9286

| |

log sample | 0.0025 | 0.0983

colog cc | 8.4014 - 10 | 8.3063 - 10

colog milli equivalent| 1.2757 | 1.2757

| ------ | ------

| 9.6796 - 10 | 9.6803 - 10

| |

Normal value HCl | .4782 | .4789

Mean | .4786 |

| |

=====================================================================

Signed

!Page D!

Date

DETERMINATION OF CHLORINE IN CHLORIDE, SAMPLE No.

=====================================================================

| |

Weight sample and tube| 16.1721 | 15.9976

| 15.9976 | 15.7117

| ------- | -------

Weight sample | .1745 | .2859

| |

Weight crucible | |

+ precipitate | 14.4496 | 15.6915

Constant weights | 14.4487 | 15.6915

| 14.4485 |

| |

Weight crucible | 14.2216 | 15.3196

Constant weight | 14.2216 | 15.3194

| |

Weight AgCl | .2269 | .3721

| |

log Cl | 1.5496 | 1.5496

log weight AgCl | 9.3558 - 10 | 9.5706 - 10

log 100 | 2.0000 | 2.0000

colog AgCl | 7.8438 - 10 | 7.7438 - 10

colog sample | 0.7583 | 0.5438

| ------- | -------

| 1.5075 | 1.5078

| |

Cl in sample No. | 32.18% | 32.20%

| |

=====================================================================

Signed

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.

Approx. Approx.

Grams relation relation

per to normal to molal

liter. solution solution

Ammonium oxalate, (NH\_{4})\_{2}C\_{2}O\_{4}.H\_{2}O 40 0.5N 0.25

Barium chloride, BaCl\_{2}.2H\_{2}O 25 0.2N 0.1

Magnesium ammonium chloride (of MgCl\_{2}) 71 1.5N 0.75

Mercuric chloride, HgCl\_{2} 45 0.33N 0.66

Potassium hydroxide, KOH (sp. gr. 1.27) 480

Potassium thiocyanate, KSCN 5 0.05N 0.55

Silver nitrate, AgNO\_{3} 21 0.125N 0.125

Sodium hydroxide, NaOH 100 2.5N 2.5

Sodium carbonate. Na\_{2}CO\_{3} 159 3N 1.5

Sodium phosphate, Na\_{2}HPO\_{4}.12H\_{2}O 90 0.5N or 0.75N 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.

A solution of ammonium molybdate is best prepared as follows: Stir

100 grams of molybdic acid (MoO\_{3}) into 400 cc. of cold, distilled

water. Add 80 cc. of concentrated ammonium hydroxide (sp. gr. 0.90).

Filter, and pour the filtrate slowly, with constant stirring, into a

mixture of 400 cc. concentrated nitric acid (sp. gr. 1.42) and 600

cc. of water. Add to the mixture about 0.05 gram of microcosmic salt.

Filter, after allowing the whole to stand for 24 hours.

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 5.6 N and 5.6 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.

Nitric acid (sp. gr. 1.20) contains 32.25 per cent HNO\_{3} by weight,

and corresponds to a 6.1 N 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 and 15.8 molal solution.

Sulphuric acid (sp. gr. 1.8354) contains 93.19 per cent H\_{2}SO\_{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\_{2}SO\_{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. 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 Density. Volume.

Centigrade.

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.

Corrections for 1 cc.

Concentration. of solution between

15° and 35°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.

INTERNATIONAL ATOMIC WEIGHTS

==========================================================

| | |

| 1920 | | 1920

\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_|\_\_\_\_\_\_\_\_\_\_

| | |

Aluminium Al | 27.1 | Molybdenum Mo | 96.0

Antimony Sb | 120.2 | Neodymium Nd | 144.3

Argon A | 39.9 | Neon Ne | 20.2

Arsenic As | 74.96 | Nickel Ni | 58.68

Barium Ba | 137.37 | Nitrogen N | 14.008

Bismuth Bi | 208.0 | Osmium Os | 190.9

Boron B | 11.0 | Oxygen O | 16.00

Bromine Br | 79.92 | Palladium Pd | 106.7

Cadmium Cd | 112.40 | Phosphorus P | 31.04

Caesium Cs | 132.81 | Platinum Pt | 195.2

Calcium Ca | 40.07 | Potassium K | 39.10

Carbon C | 12.005 | Praseodymium Pr | 140.9

Cerium Ce | 140.25 | Radium Ra | 226.0

Chlorine Cl | 35.46 | Rhodium Rh | 102.9

Chromium Cr | 52.0 | Rubidium Rb | 85.45

Cobalt Co | 58.97 | Ruthenium Ru | 101.7

Columbium Cb | 93.1 | Samarium Sm | 150.4

Copper Cu | 63.57 | Scandium Sc | 44.1

Dysprosium Dy | 162.5 | Selenium Se | 79.2

Erbium Er | 167.7 | Silicon Si | 28.3

Europium Eu | 152.0 | Silver Ag | 107.88

Fluorine Fl | 19.0 | Sodium Na | 23.00

Gadolinium Gd | 157.3 | Strontium Sr | 87.63

Gallium Ga | 69.9 | Sulphur S | 32.06

Germanium Ge | 72.5 | Tantalum Ta | 181.5

Glucinum Gl | 9.1 | Tellurium Te | 127.5

Gold Au | 197.2 | Terbium Tb | 159.2

Helium He | 4.00 | Thallium Tl | 204.0

Hydrogen H | 1.008 | Thorium Th | 232.4

Indium In | 114.8 | Thulium Tm | 168.5

Iodine I | 126.92 | Tin Sn | 118.7

Iridium Ir | 193.1 | Titanium Ti | 48.1

Iron Fe | 55.84 | Tungsten W | 184.0

Krypton Kr | 82.92 | Uranium U | 238.2

Lanthanum La | 139.0 | Vanadium V | 51.0

Lead Pb | 207.2 | Xenon Xe | 130.2

Lithium Li | 6.94 | Ytterbium Yb | 173.5

Lutecium Lu | 175.0 | Yttrium Y | 88.7

Magnesium Mg | 24.32 | Zinc Zn | 65.37

Manganese Mn | 54.93 | Zirconium Zr | 90.6

Mercury Hg | 200.6 | |

==========================================================

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